Room Temperature Superconductor WORKSHOP

Wednesday, 20 June, 2007

Struggle to find higher-T_c materials

Jun Akimitsu

Department of Physics and Mathematics,
Aoyama Gakuin University

Akimitsu Lab. HP
URL http://www.phys.aoyama.ac.jp/~w3-jun/

Wednesday, 20 June, 2007

Desperate Struggle to find higher-T_c materials

Jun Akimitsu

Department of Physics and Mathematics,
Aoyama Gakuin University

Akimitsu Lab. HP
URL http://www.phys.aoyama.ac.jp/~w3-jun/

Many approaches to higher-T_c superconductors

1) **Carrier-doped CuO_2 planes**

- Unidentified Superconducting Objects -

- Extremely large energy gap observed by STM -

2) Cu-oxides having a different crystal structure

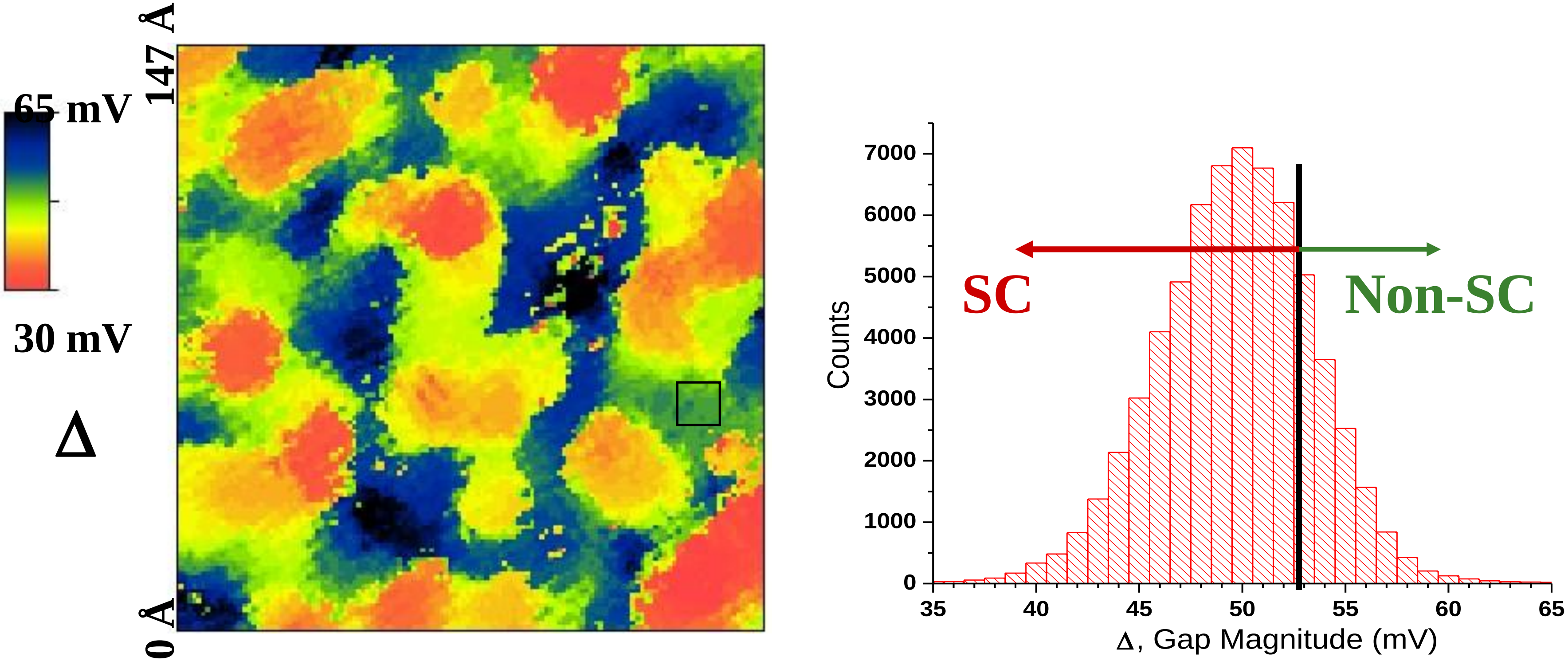
-Ladders-

-Lieb model- etc…

3) Metal superconductors including
light elements (boron, carbon etc…)

4) Carrier-doped clusters / nanotubes

Intrinsic inhomogeneity in CuO_2 plane

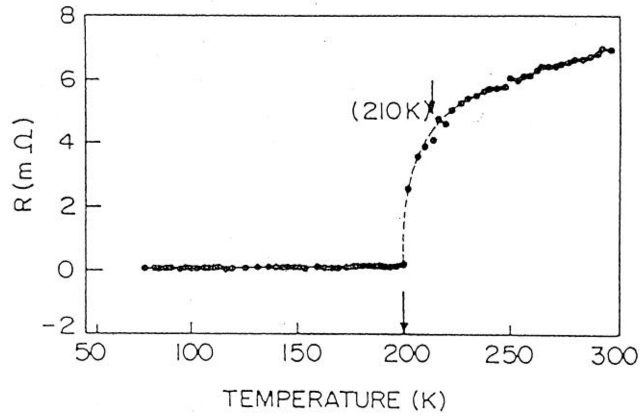


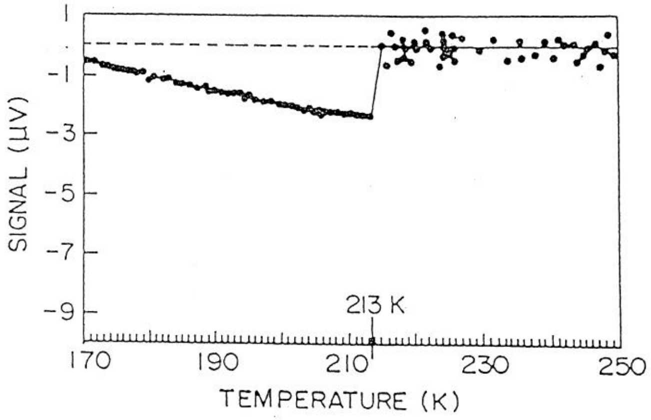
Extremely large SC gap was observed by STM.

By J.C. Davis and S. Uchida

Unidentified Superconducting Objects

- In an early stage, after the discovery of high-T_c cuprate, a lot of Unidentified Superconducting Object (USO) has been found.
- Are all data USO ?





Many approaches to higher-T_c superconductors

1) Carrier-doped CuO_2 planes

- Unidentified Superconducting Objects –
- Extremely large energy gap observed by STM -

2) **Cu-oxides having a different crystal structure**

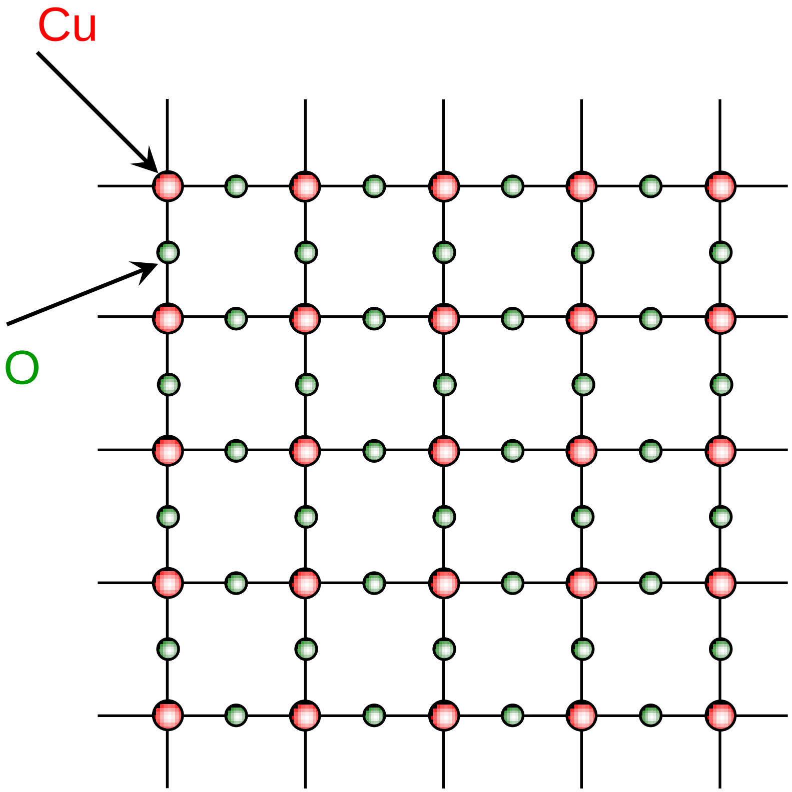
-Ladders-

-Lieb model- etc…

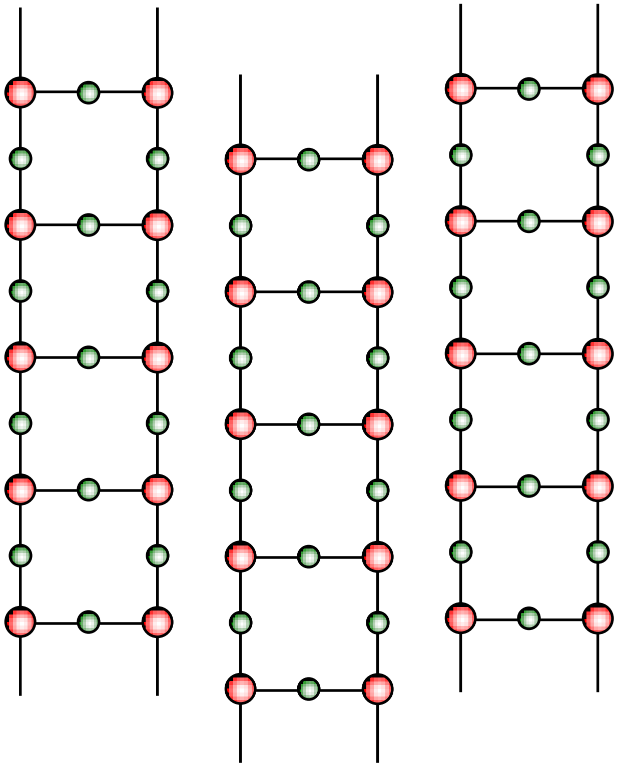
3) Metal superconductors including
light elements (boron, carbon etc…)

4) Carrier-doped clusters / nanotubes

CuO$_2$ 2D-plane is essential for high-T_c superconductivity or not ?



CuO$_2$ 2D plane

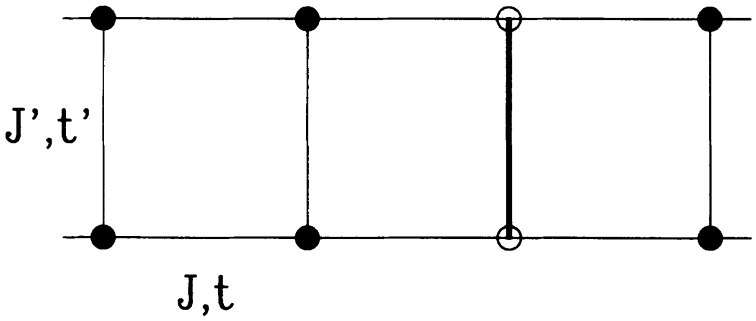


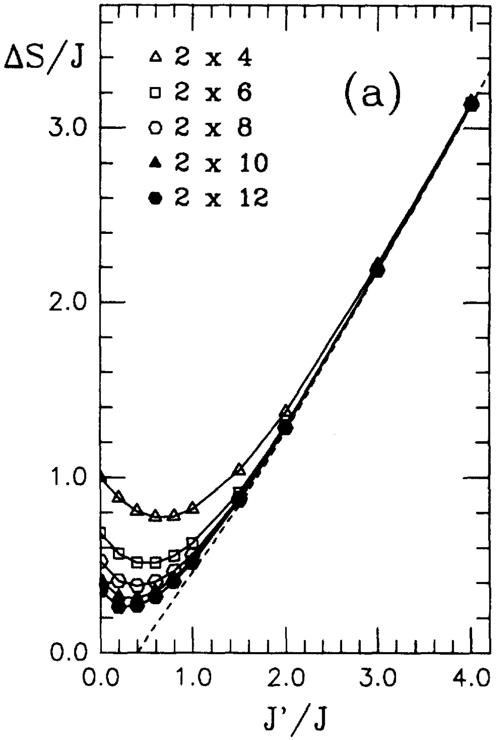
2-leg ladder

By M. Takano *et al*. (Kyoto)

Theoretical Prediction of Superconductivity in Ladder Compounds

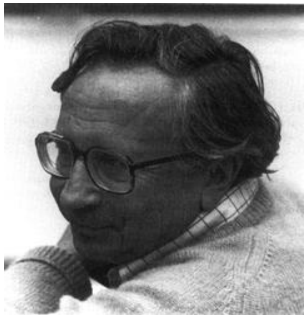
- Superconductivity in ladders and coupled planes
  - T.M. Rice *et al.*,
    - Europhys. Lett. 23 (1993) 445.
  - E. Dagotto *et al.*,
    - Phys. Rev. B <u>45</u> (1992) 5744.
  - Superconductivity appears and spin gap still exists in an even number-leg ladder.





Digression

Matthias Law



Bernd Matthias

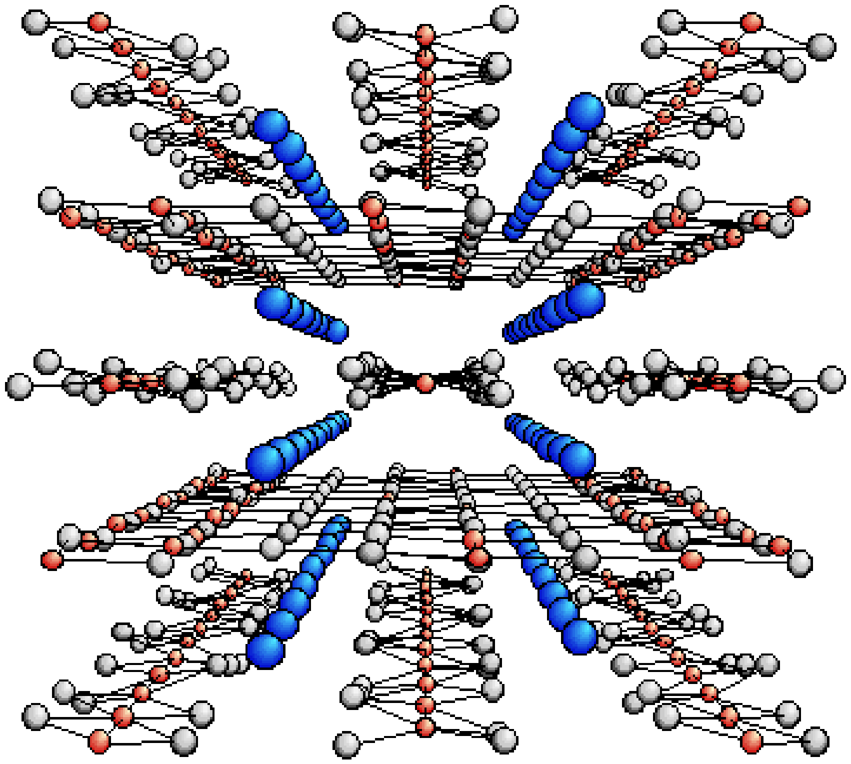
B.T. Matthias

- 1^{st} law: To find materials with large $N(0)$
- 2^{nd} law: Do not believe theorist's prediction
- Akimitsu Law: Pretend to believe theorist's prediction

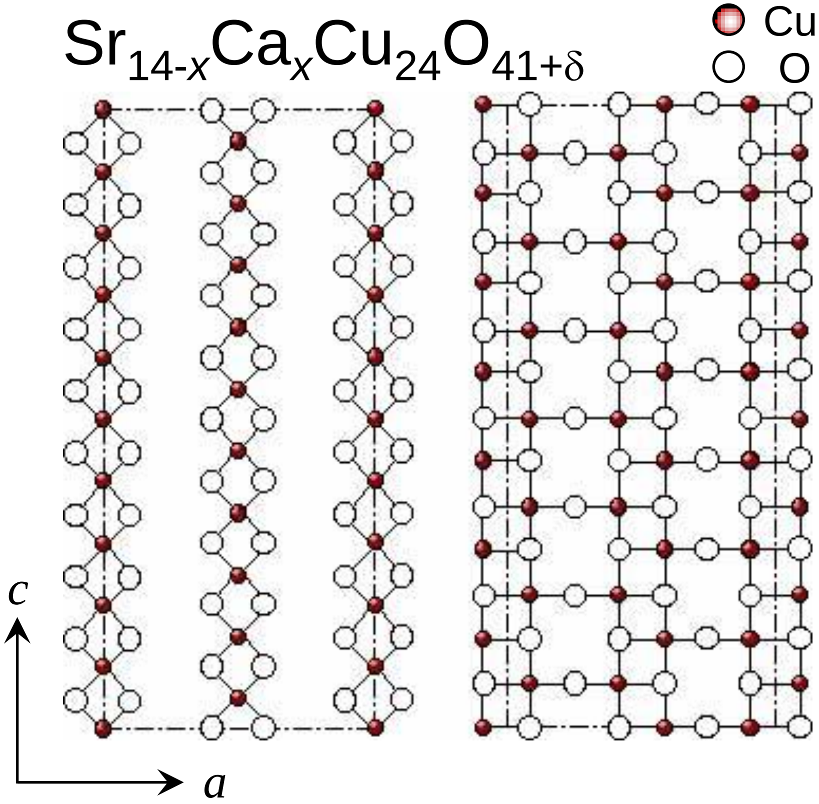
Picture: National Academy of Sciences

Ladder-system

Telephone number compound 14 - 24 - 41



$Sr_{14-x}Ca_xCu_{24}O_{41+\delta}$



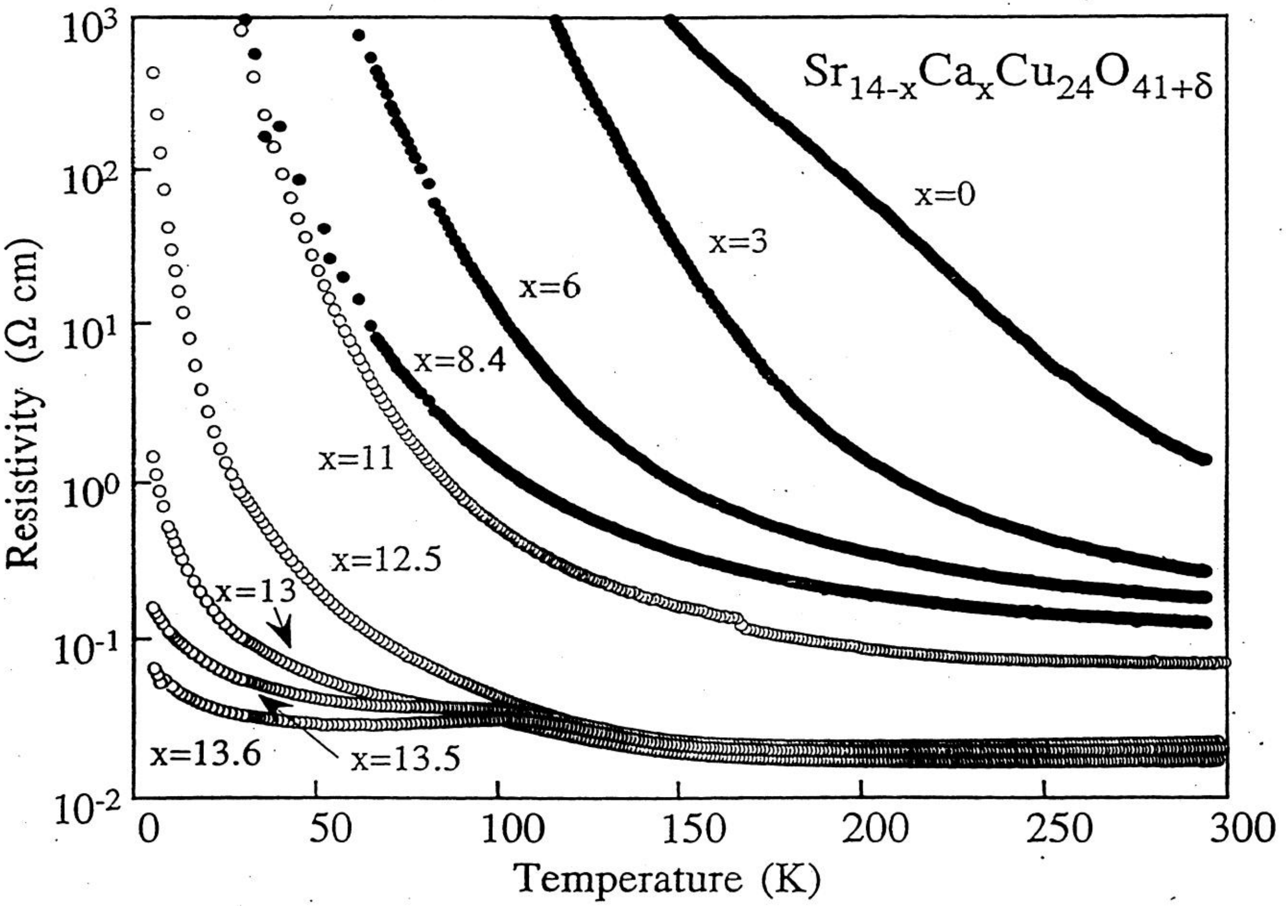
1D-chain layer

(CuO_2)

2-leg ladder layer

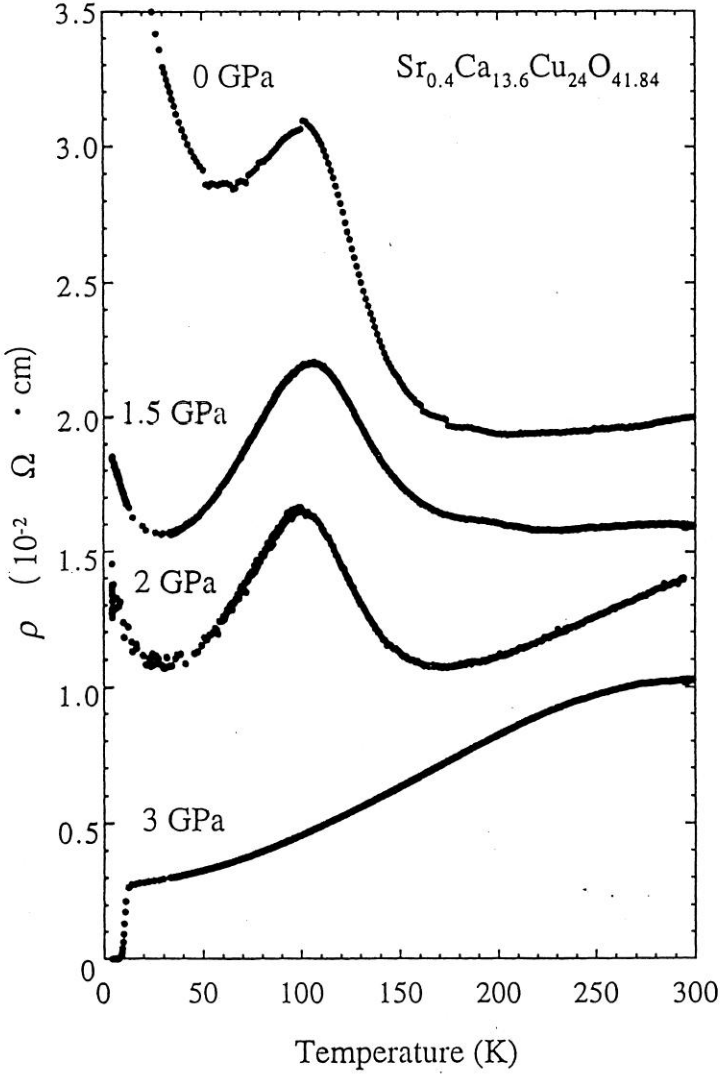
(Cu_2O_3)

Decrease of the resistivity by Ca-doping



M. Uehara *et al*., J. Phys. Soc. Jpn. **65** (1996) 2764

Superconductivity in 2-leg ladder compound



M. Uehara and

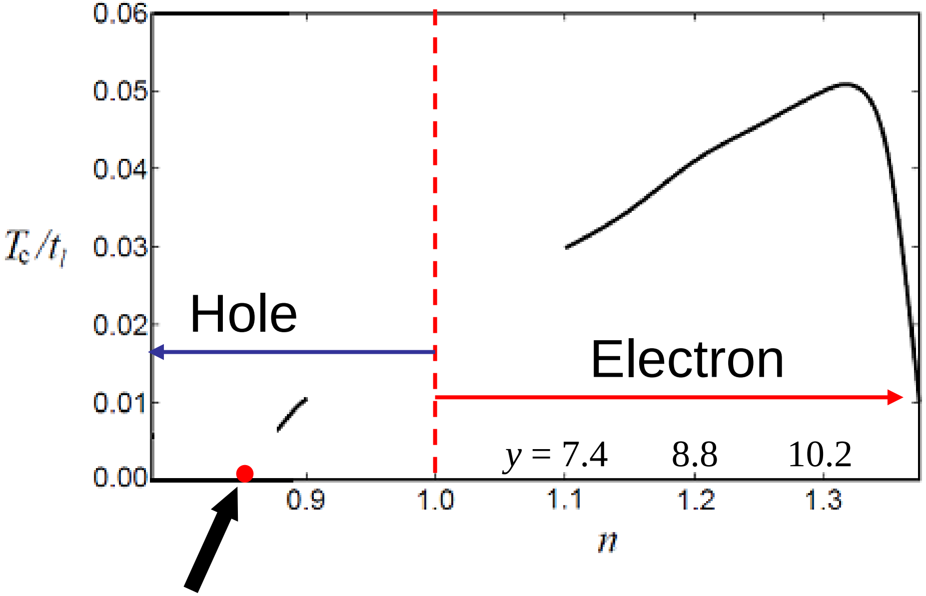
Y. Nagata

M. Uehara *et al*., J. Phys. Soc. Jpn. **65** (1996) 2764

Electron doping to ladder compound

- FLEX calc.
  - Hole-type
    - T_c~12K
  - Electron-type
    - **T_c~600K(!)**

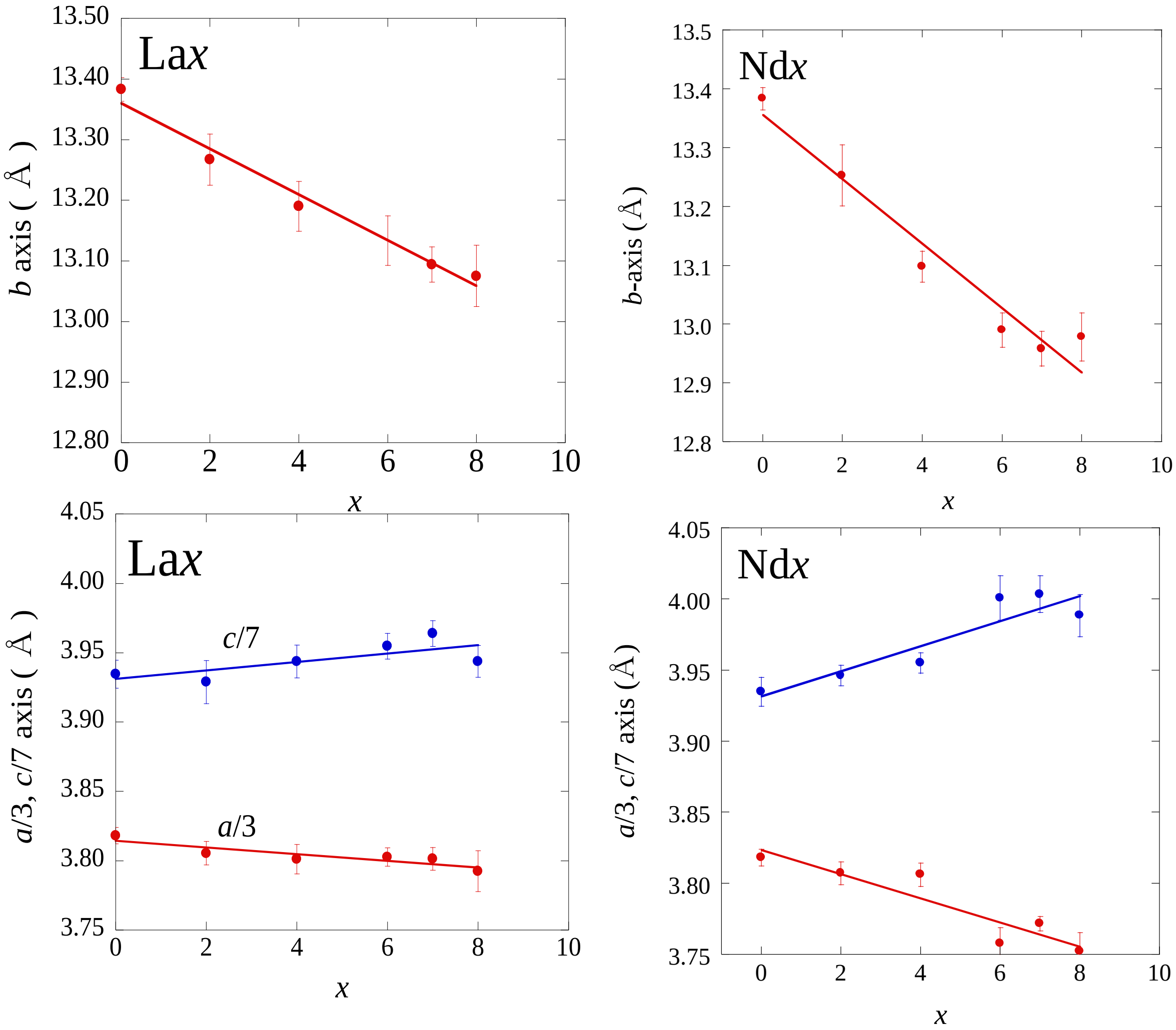
- Trial for electron-doping
  - $Sr_{14-x}La_xCu_{24}O_{41}$
  - $Sr_{14-x}Nd_xCu_{24}O_{41}$

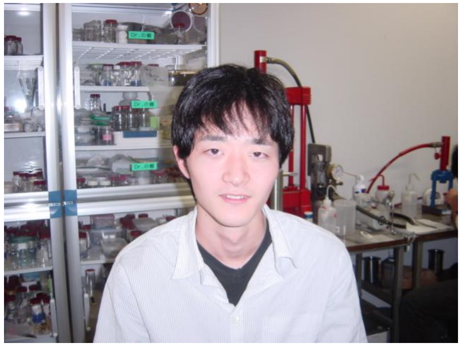


$T_c/t_l = 0.001$

K. Kuroki et al., Phys. Rev. B 72, 212509 (2005)

La, Nd doping dependence of lattice constants

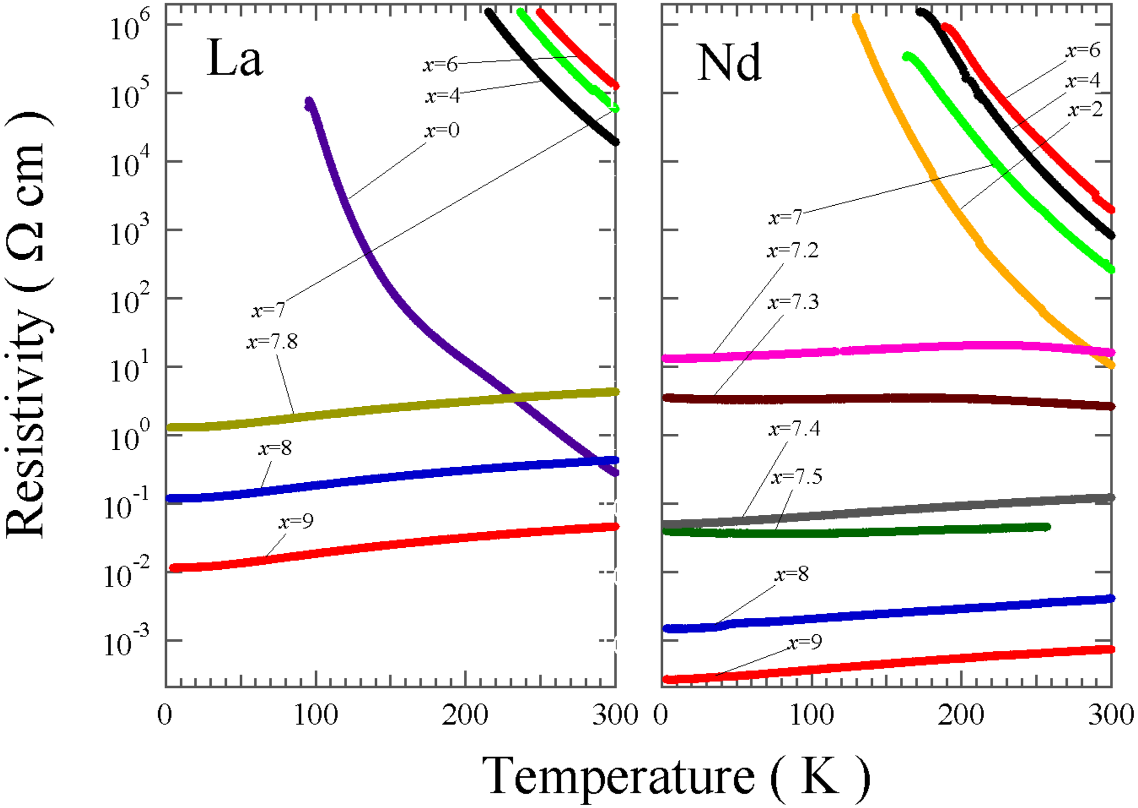




Y. Sugiyama

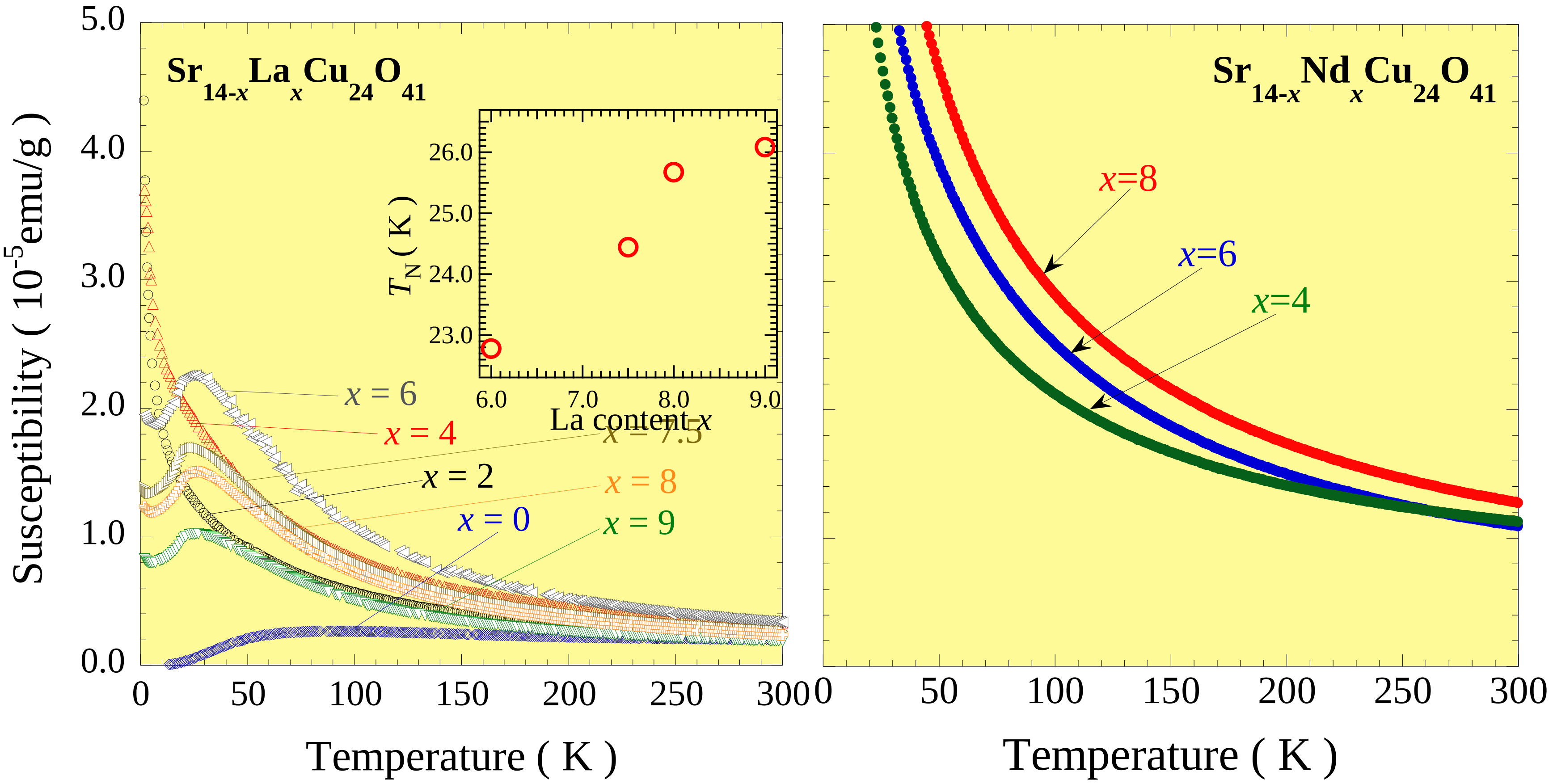
- Lattice constant *b* is decreased by La, Nd-doping.

Temperature dependence of resistivity



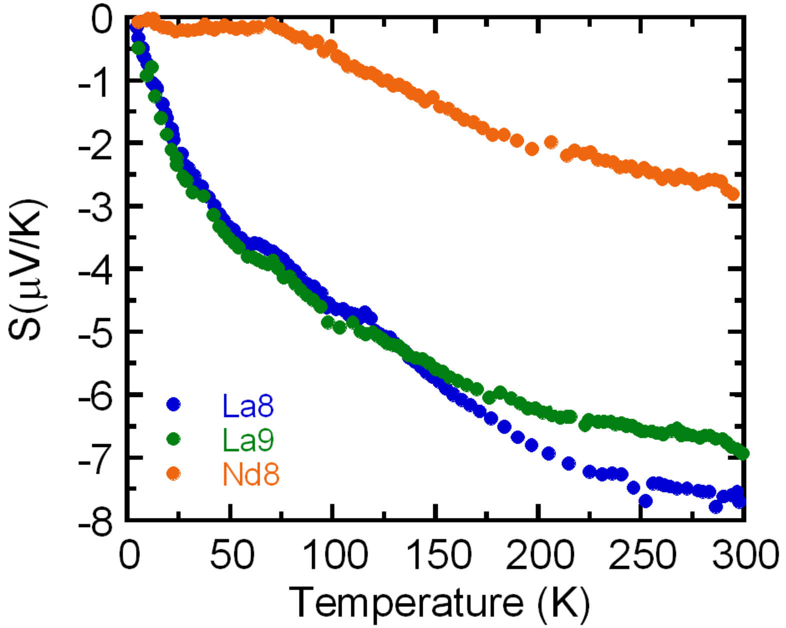
- $(Sr,La,Nd)_{14}Cu_{24}O_{41}$ system shows a metal-insulator transition.
  - No sign of superconductivity.

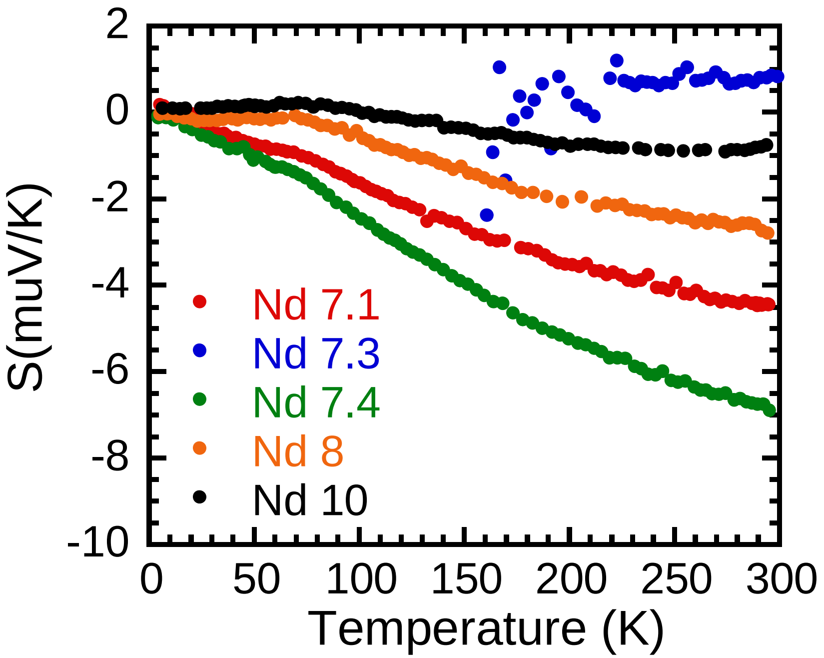
Temperature dependence of susceptibility



- The magnetic ground state of composition between $x = 6$ and 9 has an antiferromagnetic ordering state.

Temperature dependence of thermopower

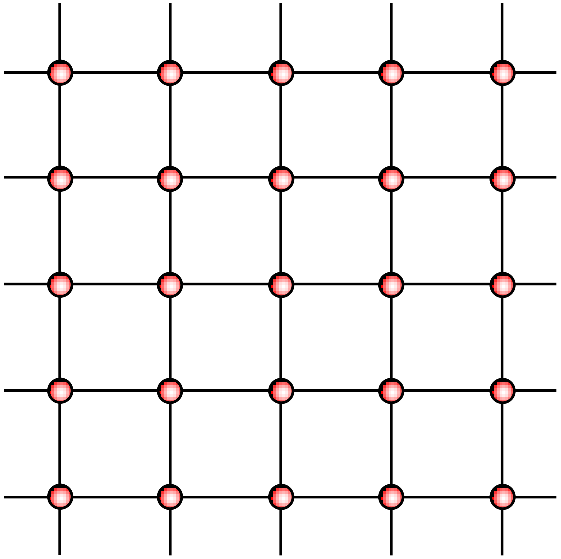




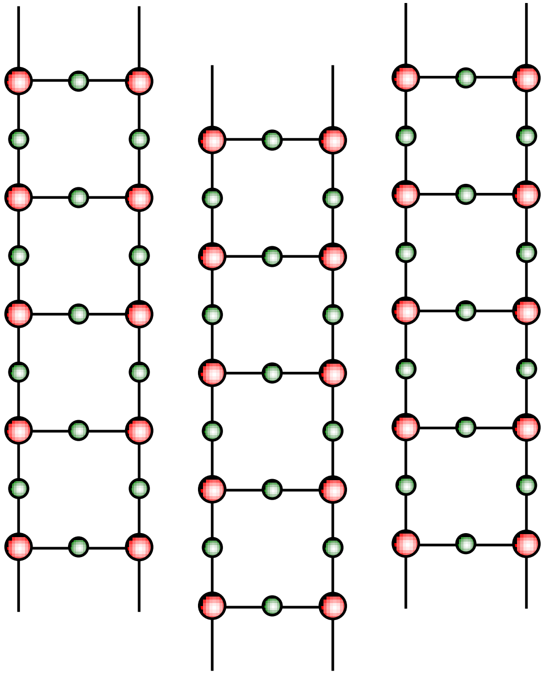
- La-doping
  - La-content dependence is very small
- Nd-doping
  - S~0 under 75K in $(Sr_6Nd_8)Cu_{14}O_{41}$

Aoyama-Gakuin University

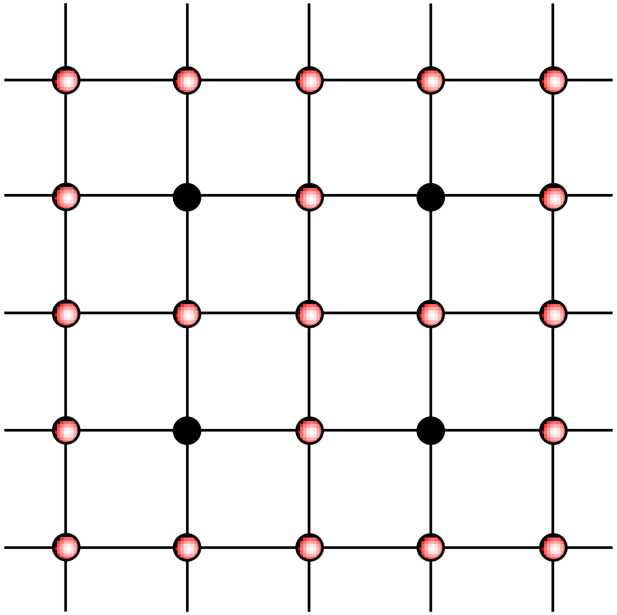
CuO_2 plane, ladder, Lieb model



CuO_2 plane



2-leg ladder



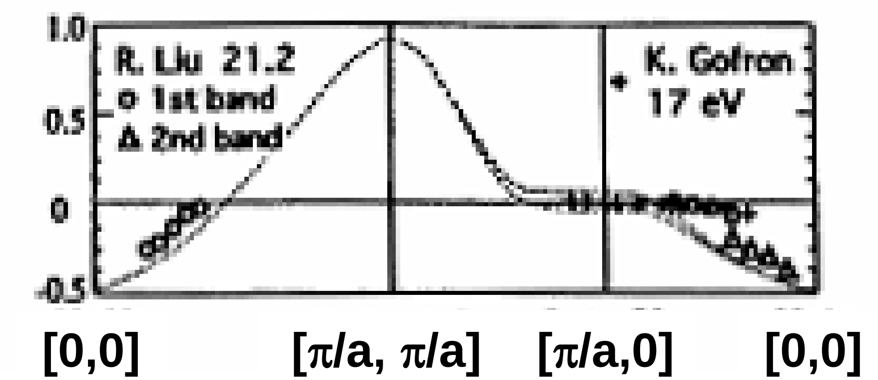
Lieb model

1/4 periodic order

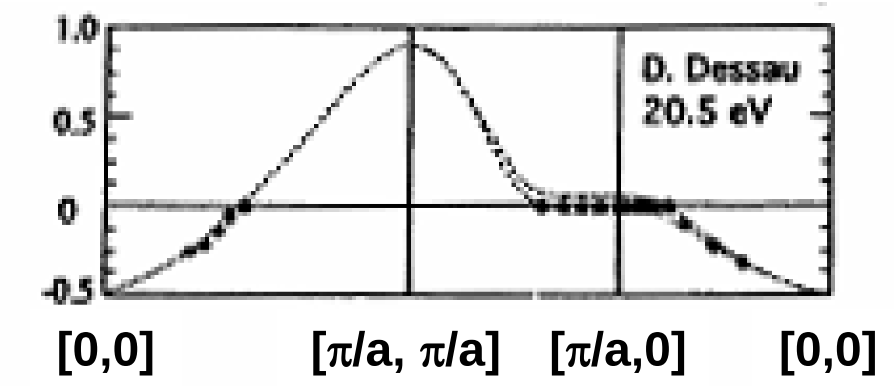
$Cu_{0.75}M_{0.25}O_2$ plane

Flat band dispersion in high-T_c cuprates (ARPES)

Y123

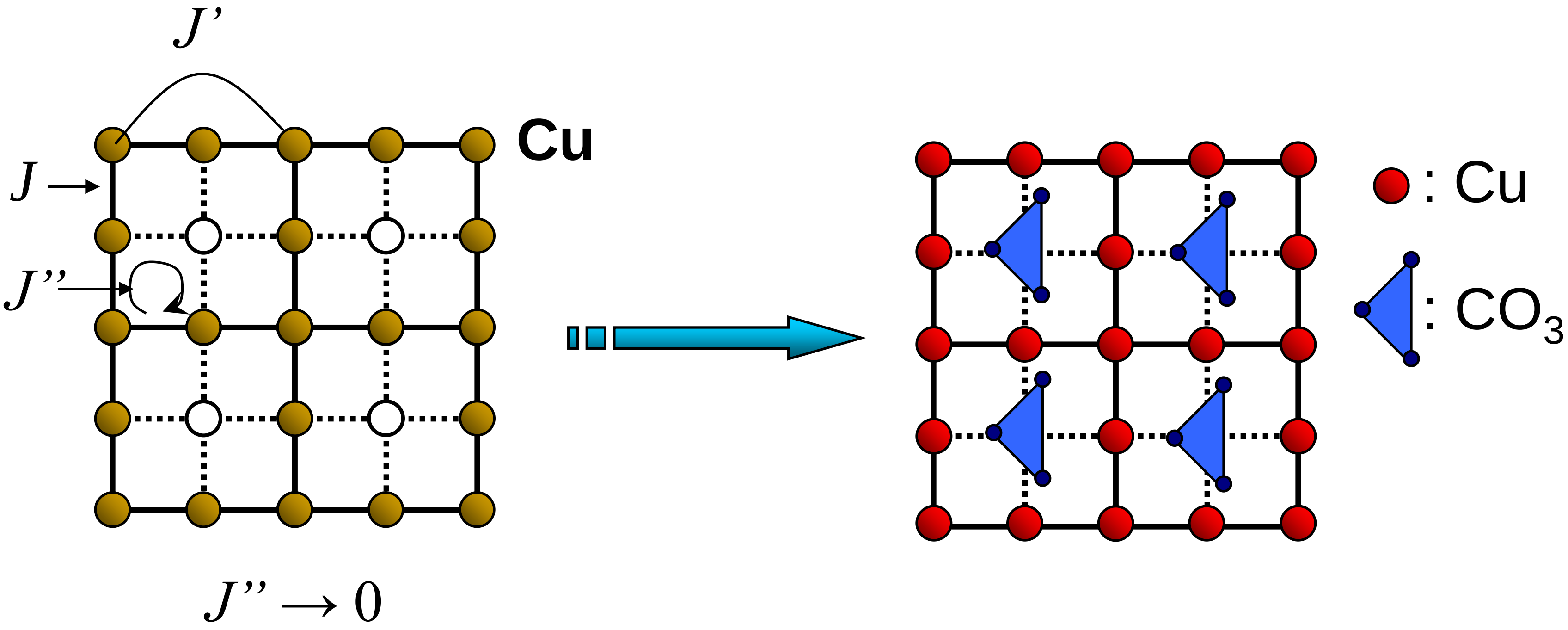


Bi2212



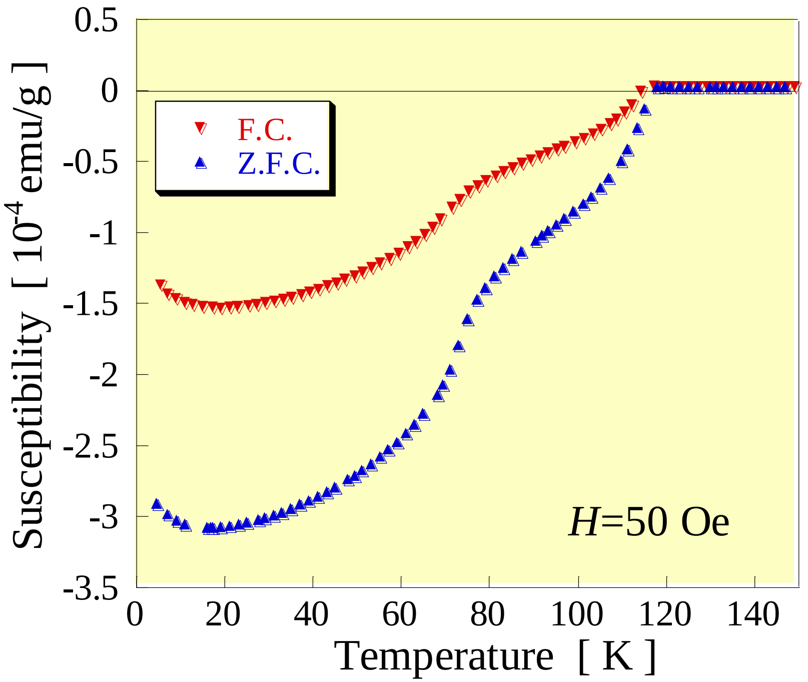
Z-X. Shen and D. S. Dessa, Phys. Rep. **253** (1995) 1.

Candidate for flat dispersion -Lieb model-



Theoretically suggested by Imada and Nagaosa

Superconductive signal in Ca-Cu-O-(CO_3) system



Ca	**Na**	***V.F.***
5.5/15	10.5/15	0.5%
5.5/15	**21/15**	**< 0.1%**
7/15	9/15	0.4%
7/15	**18/15**	**< 0.1%**
4/15	12/15	—
4/15	**24/15**	**< 0.1%**
7.5/15	8.5/15	0.2%
7.5/15	**17/15**	**0.3%**
13/15	3/15	—
13/15	**15/15**	**0.8%**

unpublished, H. Ozaki, T. Suzuki, K. Horigane, Y. Zenitani and J. Akimitsu

Many approaches to higher-T_c superconductors

1) Carrier-doped CuO_2 planes
   - Unidentified Superconducting Objects –
   - Extremely large energy gap observed by STM -

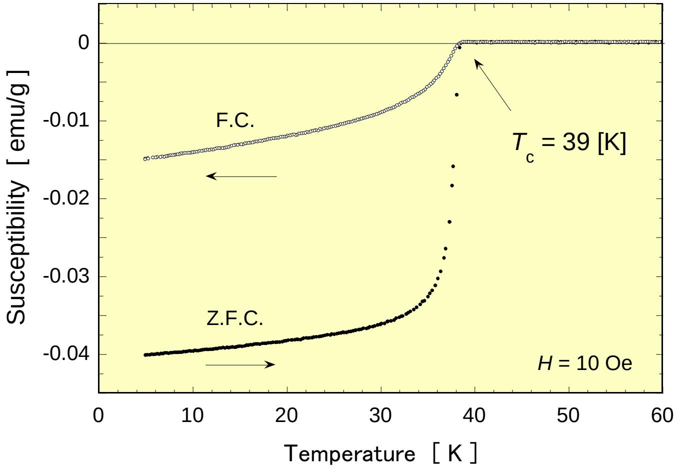
2) Cu-oxides having a different crystal structure
   - Ladders -
   - Lieb model - etc…

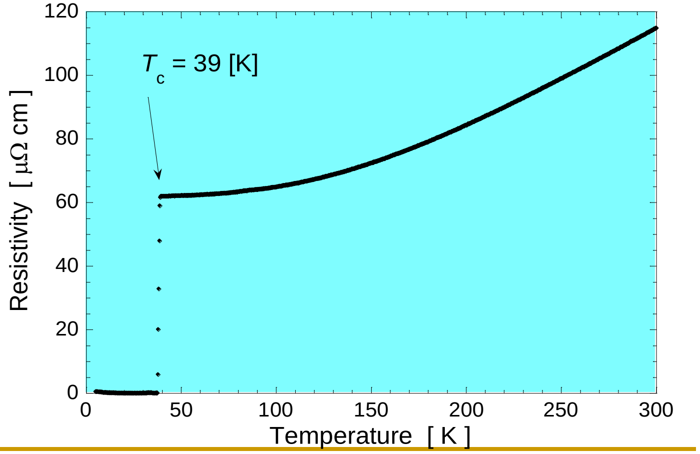
3) **Metal superconductors including light elements (boron, carbon etc…)**

4) Carrier-doped clusters / nanotubes

Are there any new metal high-T_c superconductors ?

Discovery of superconductivity in MgB_2



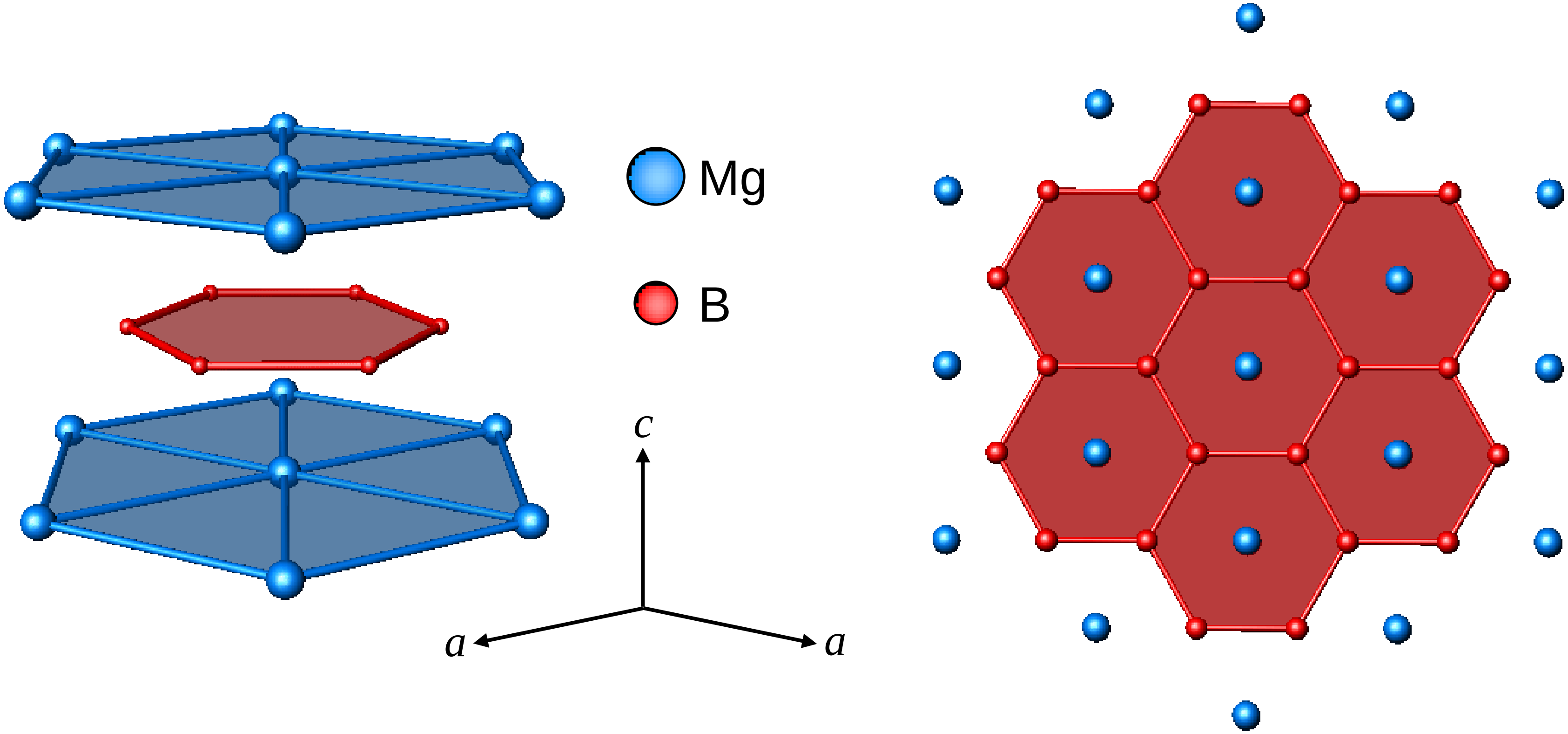


J. Nagamatsu, N. Nakagawa,

T. Muranaka and Y. Zenitani

Crystal structure of MgB$_2$

Characteristic 2D structure（honeycomb lattice）



J. Nagamatsu *et al*., Nature **410** (2001) 63

Genie in a bottle

Robert J. Cava

An overlooked compound has a surprise in store for physicists. It becomes superconducting at a much higher temperature than any other stable metallic compound.

The field of superconductivity has been rocked by a startling announcement. For fifteen years, researchers have been delving into the mysterious and complex world of high-temperature superconducting materials Ñ virtually ignoring simple metallic compounds because they superconduct at very low temperatures. But now Akimitsu and colleagues have discovered superconductivity at an amazing 39 degrees above absolute zero in the simple compound magnesium boride (MgB_2). They report their discovery on page 63 of this issue[1], in what must be one of the shortest communications published in Nature in recent memory.

Superconductors are materials that lose their resistance to electrical current flow below a certain critical temperature (T_c). In the ideal case, this zero-resistance state is absolute Ñ electrons flowing in a continuous loop of superconducting wire below T_c could theoretically flow for the age of the Universe and never lose any energy. But in the real world there are losses from microscopic inhomogeneities, for example, and the ideal is never truly obtained.

Nonetheless, devices made with superconducting materials have resistances that are orders of magnitude lower than those of devices made with the best conventional conductors. This low resistance to current flow means that large currents (on the order of 10^6 amperes per square centimetre of wire cross-section) can be passed without significant heating. The magnets in magnetic resonance imaging instruments now in common use, for example, are made from metal-alloy superconducting wires. These magnets are cooled below the T_c of the metal alloy by immersion in liquid helium at 4.2 K. One can sometimes see trucks delivering helium to hospital loading docks for that purpose.

Almost exactly 15 years ago, physicists were stunned by the announcement that a ceramic composed of barium, yttrium, copper and oxygen could become superconducting at temperatures above that of liquid nitrogen (77 K)[2]. This discovery, based on a modification of a formula first announced by Bednorz and MŸller[3] who later won the Nobel Prize for physics, sparked an explosion in condensed-matter physics and materials-science research, and the echo can still be heard. It is difficult to describe the feeling that we had for the infinite possibilities promised by that discovery. Imagine a world with perpetual engines, trains that magnetically ÒfloatÓ above the tracks and ultrafast computers. For the people in the thick of it, it was almost impossible to sleep for years afterwards Ñ every minute spent sleeping was another minute missed in trying to figure out the implications of a whole new way of thinking about the world. Some of the promises of those early days have been fulfilled, and the legacy of the discovery of high-temperature superconductivity has been to change forever the culture of multidisciplinary research in the physical sciences.

Akimitsu apparently announced the discovery of superconductivity in MgB_2 (ref. 1) at a conference in Sendai, Japan, in early January. The story came to my attention a few weeks later, through what must have been a convoluted path of e-mails and word-of-mouth. The whole process is hauntingly reminiscent of the way such stories came to light in the early days of high-temperature superconductivity Ñ under the guise of a narrative seemingly too fantastic to be true, and yet at the same time, too fantastic to be entirely false.

The story I heard was that Akimitsu and his group were attempting to make a chemical analogue of CaB_6 Ñ a semiconducting material that surprisingly becomes ferromagnetic (like iron) when doped with a small amount of electrons[4]. They tried to replace calcium with magnesium, which is directly above it in the periodic table. One of their starting materials was the simple compound MgB_2, which has been known since 1953 and is available in kilogram-size bottles from suppliers of inorganic chemicals (Fig. 1). MgB_2 is one of the common reagents used in metathesis reactions (in which compounds exchange partners)[5], and magnesium borides are used in some commercial preparations of elemental boron. Apparently, the stuff they got out of the bottle became superconducting at 39 K, 16 K higher than any other simple metallic compound. That must have been quite a shock.

But why the excitement? After all, critical temperatures for the high-temperature copper oxides have risen to 160 K over the years, four times the value for MgB_2. There are two reasons for the fuss. First, early indications[6] are that this material appears to become superconducting by what is known as the BCS mechanism (named after its discoverers, Bardeen, Cooper and Schrieffer)[7], in which the interactions between the electrons that give rise to superconductivity are mediated by thermal vibrations of the atoms in the underlying crystal lattice. So, unlike the high-temperature copper oxide superconductors, MgB_2 is likely to be a ÔconventionalÕ superconductor Ñ the rules of physics do not need to be bent for superconductivity to occur. MgB_2 has the highest T_c known for a chemically stable, bulk compound of this kind. This holds tremendous promise for

Figure 1 The newly discovered superconductor magnesium boride has been available in large quantities from suppliers of inorganic chemicals for many years, but physicists have finally ÔrubbedthelampÕ and found that magnesium boride superconducts at an amazing 39K (ref. 1).

“Genie in a bottle”

MgB_2 is a commercial product !!

MB_2-type Borides

Bernd Matthias

Bernd Theodor Matthias

	BeB_2											
	MgB_2											AlB_2
		ScB_2	TiB_2	VB_2	CrB_2	MnB_2						
		YB_2	ZrB_2	NbB_2	MoB_2	TcB_2	RuB_2					
	BaB_2		HfB_2	TaB_2	WB_2	ReB_2	OsB_2					

LuB_2	
UB_2	PuB_2

CrB_2 $T_N = 86$ K (J.Castaing *et all. J.Phys.Chem.Solids* (1972) Vol.33 533)

MnB_2 $T_C = 143$ K (L.Andersson *et all. Solid State Communications* Vol.4 77 (1966))

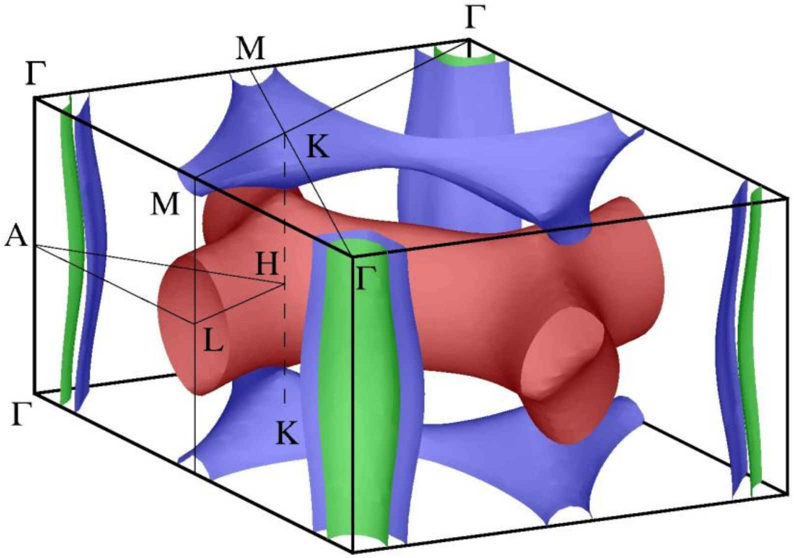
TaB_2 $T_c = 0.42$ K

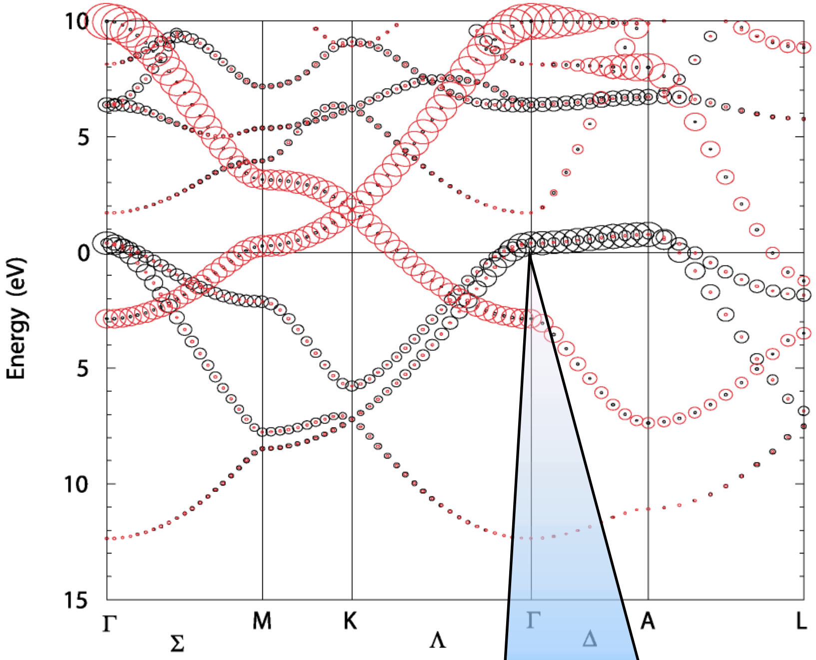
NbB_2 $T_c = 0.62$ K (L.Leyarovska *et all. J.Less-common Metals* 67 (1979) 249)
T_c= 2.2-9.4 K (A. Yamamoto *et al*., H. Takagiwa *et al*.)

Picture: National Academy of Sciences

Aoyama-Gakuin University

Fermi surface and band structure of MgB_2





Hole–like surface

Green and **Blue** cylinder ($p_{x,y}$ bands)

Blue tubular network (p_z bands)

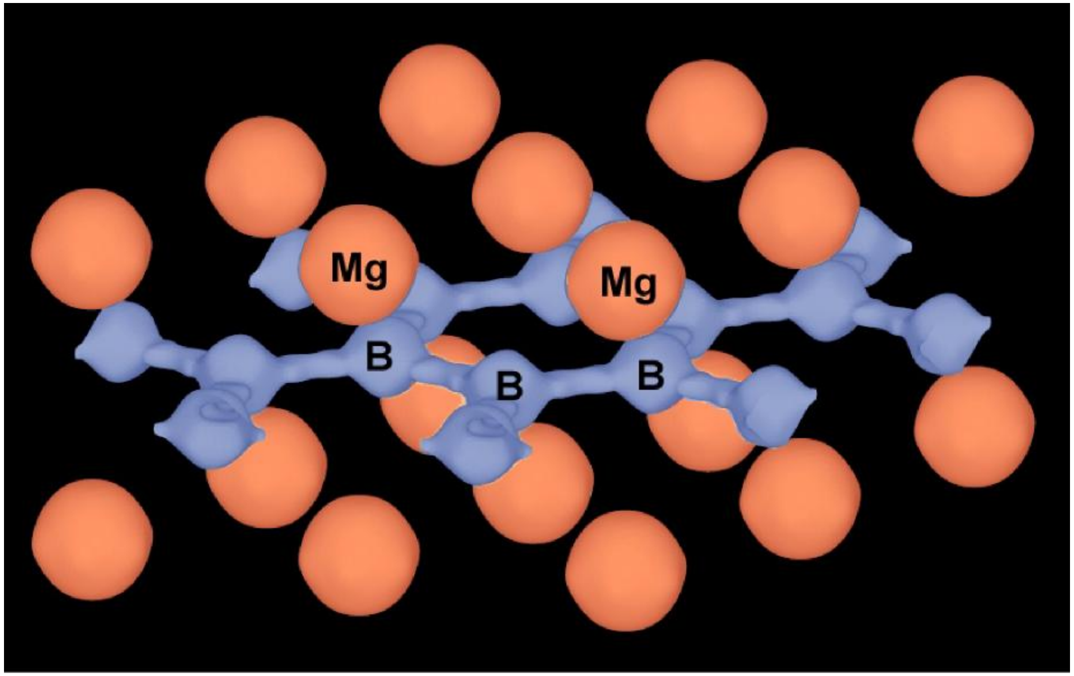
Electron–like surface

Red tubular network (p_z band)

σ band place at near E_F and degenerate at Γ-A line

J. Kortus *et al*., PRL **86** (2001) 4656

The MEM charge density in MgB_2



T=15 K

① B atoms form 2D network

② Mg atoms are isolated

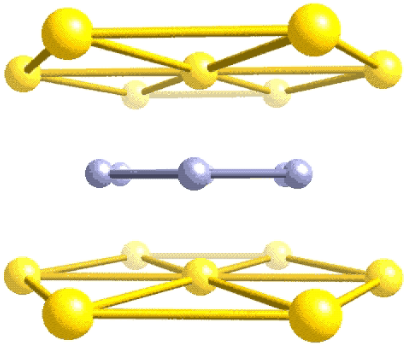
E. Nishibori *et al.*, Bonding Nature in MgB_2, JPSJ **70** (2001) 2252

Summary of MgB_2

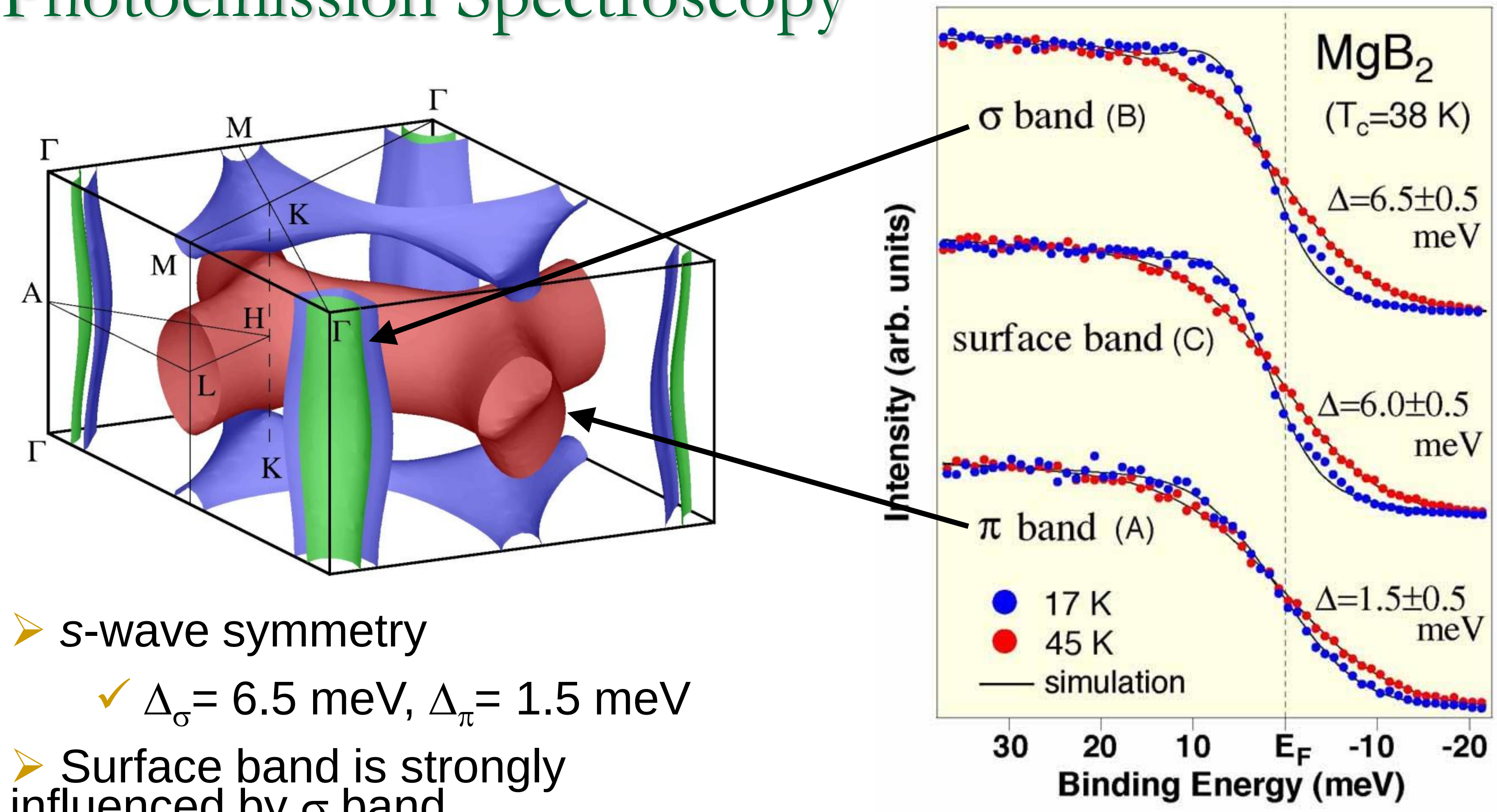
- The superconductivity can be basically explained by BCS theory
  - conventional superconductor

- The strong electron-phonon interaction due to the lattice vibration (E_{2g} phonon) in a boron-plane
  - strongly connected with the band

- The 2-gap superconductor
  - strong and weak coupling pairing in the σ, π band
  - The **"text book material"** for 2-gap superconductors



The energy gaps of MgB_2 observed by Photoemission Spectroscopy

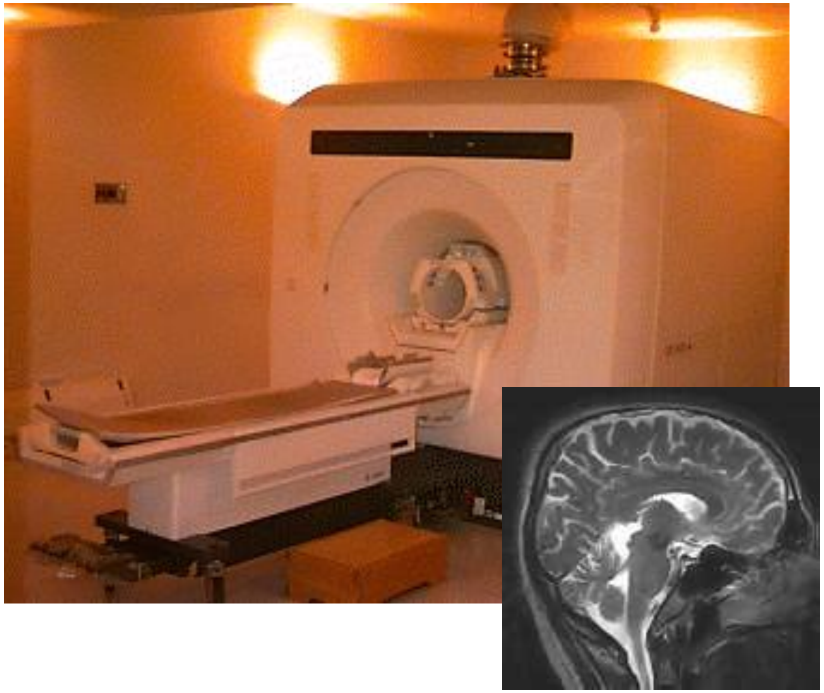


- *s*-wave symmetry
  - ✓ Δ_σ= 6.5 meV, Δ_π= 1.5 meV
- Surface band is strongly influenced by σ band.
  - ✓ gap value is close to Δ_σ (proximity effect ?)

SC gap includes two gaps.

S. Souma *et al.*, *Nature* **423** (2003) 65

Application of MgB_2



MRI (Magnetic Resonance Imaging)

LINEAR EXPRESS

Kumakura’s Group

Superconducting Material Center

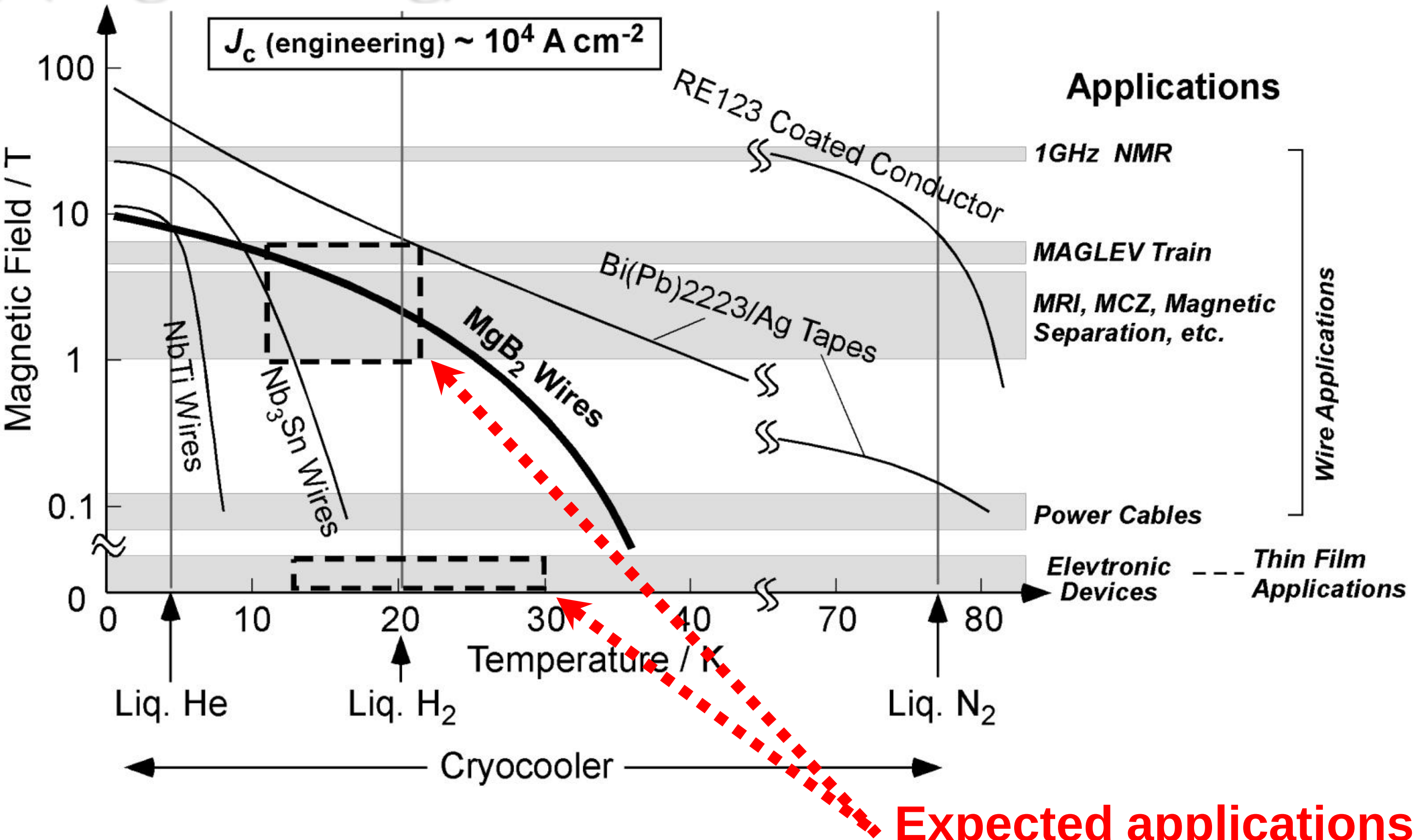
National Institute for Materials Science

Okada’s Group

Hitachi Research Laboratory

Hitachi, Ltd.

Applied fields for superconductors versus J_c (engineering) ~10^4 A/cm^2 lines

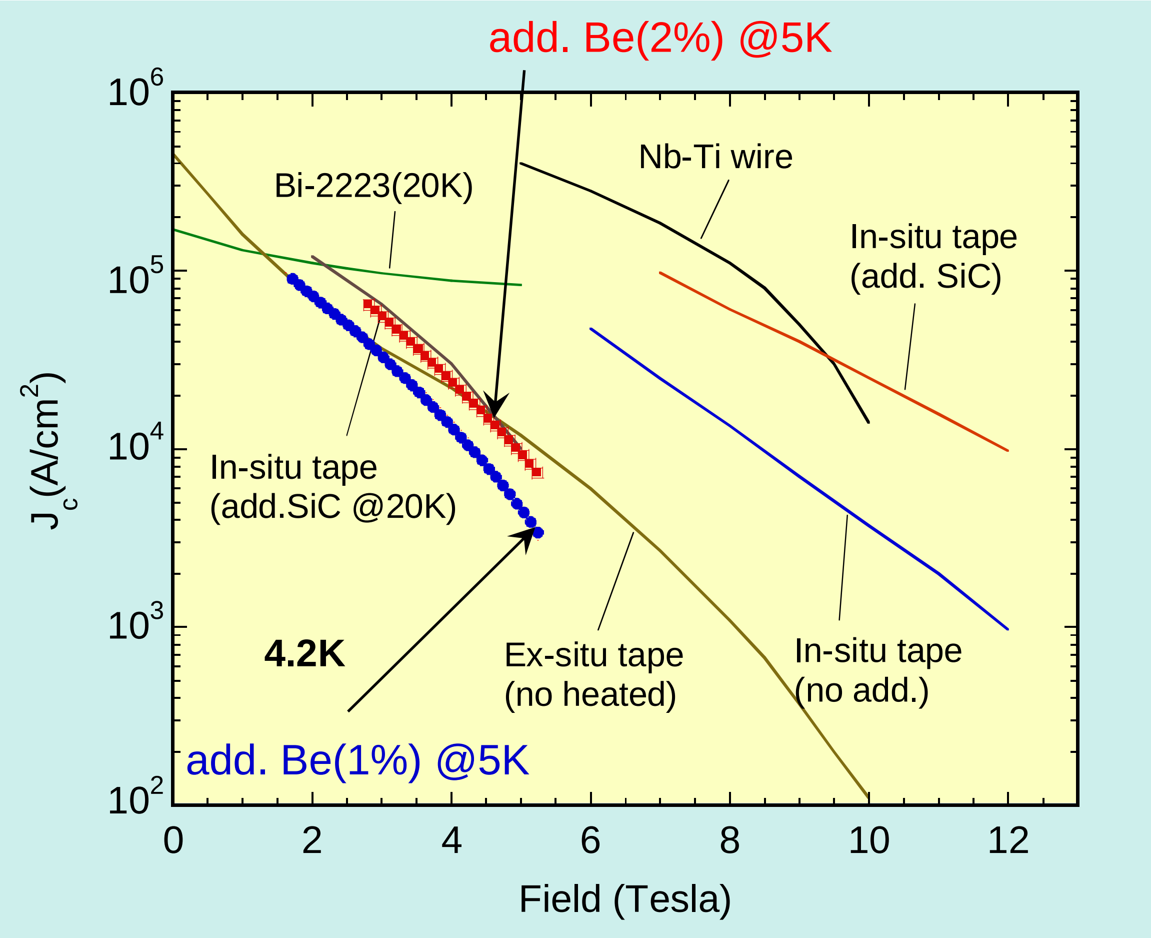


Expected applications of MgB_2 wire and thin films.

J. Shimoyama *et al.*

Aoyama-Gakuin University

Trial for enhancement of J_c in MgB_2



Adding small amount of Be

$3.0 \times 10^4 A/cm^2$

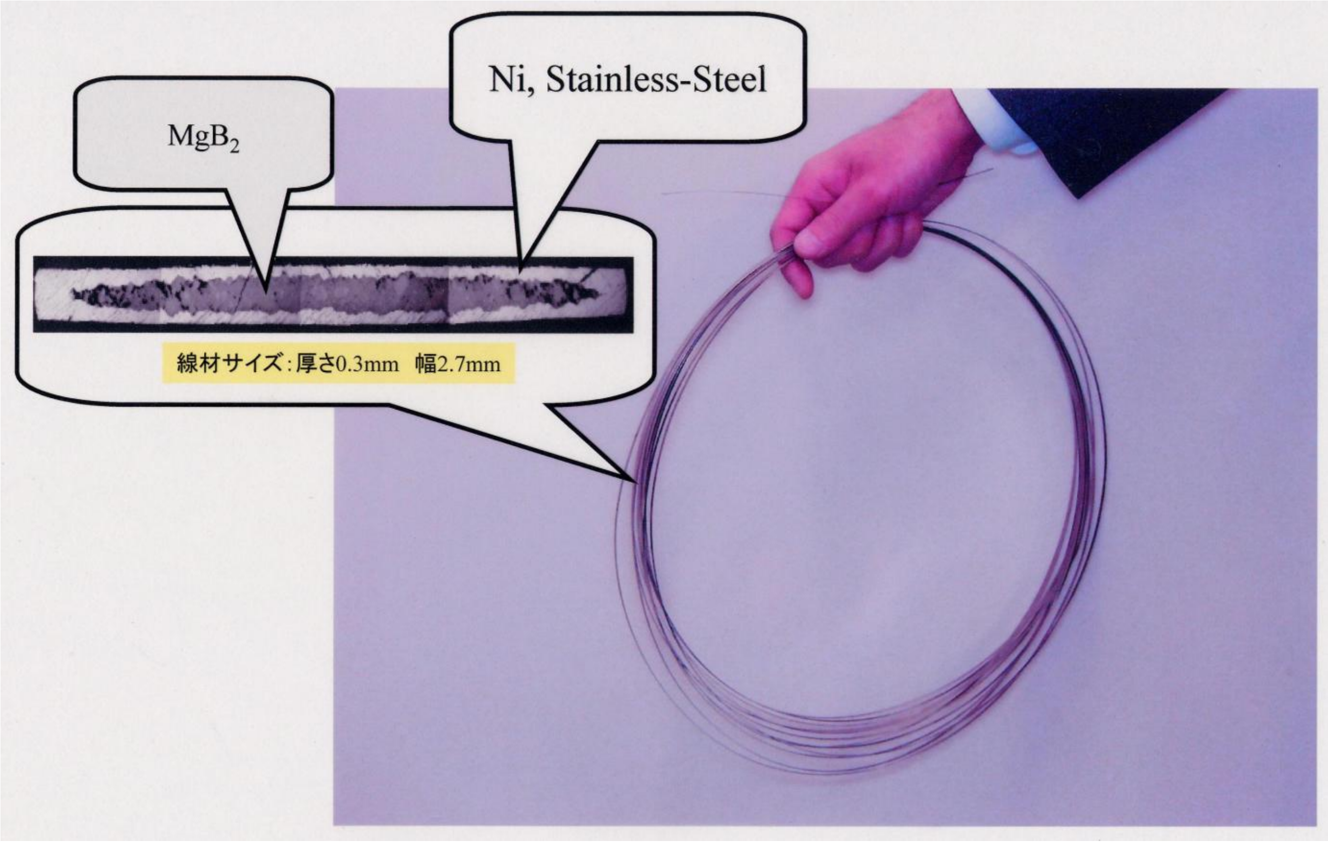
@5K, 4T

<u>The highest level *Jc* in the world</u> was achieved.

We are trying to achieve enhancement of J_c in high field region.

10m class wire of MgB_2

Successfully processed MgB_2 coil at the first time in the world !!

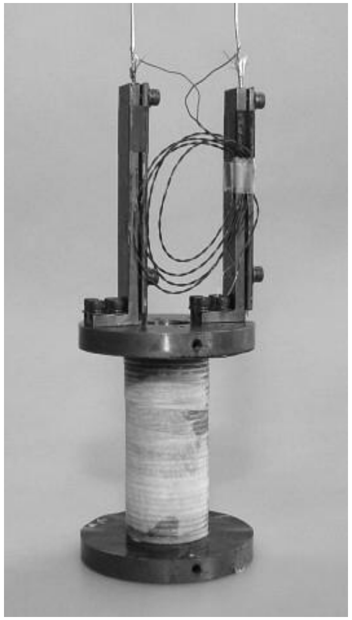


Establishment of processing is near completion.

Hitachi Research Laboratory, Hitachi Ltd.
National Institute for Materials Science

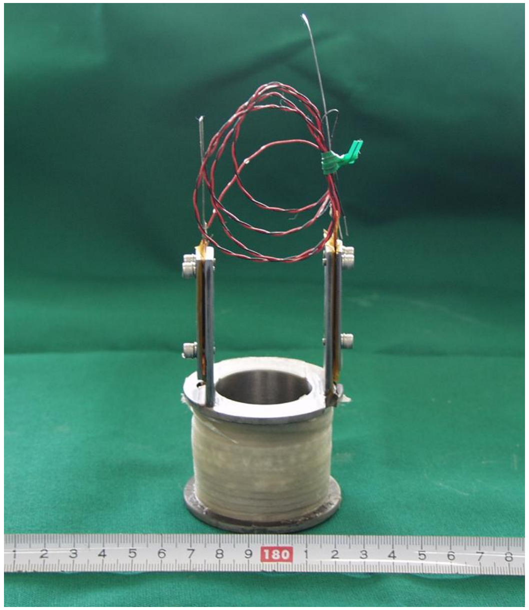
Trial product of small magnet using MgB_2

1^{st} machine



Diameter： 43mm
Field： 0.13T(4.2K,0T)

2^{nd} machine



Diameter： 48mm
Field： 0.5T(4.2K, 0T)

We succeeded in fabricating the SC magnet by MgB_2 at the first time in the world !!

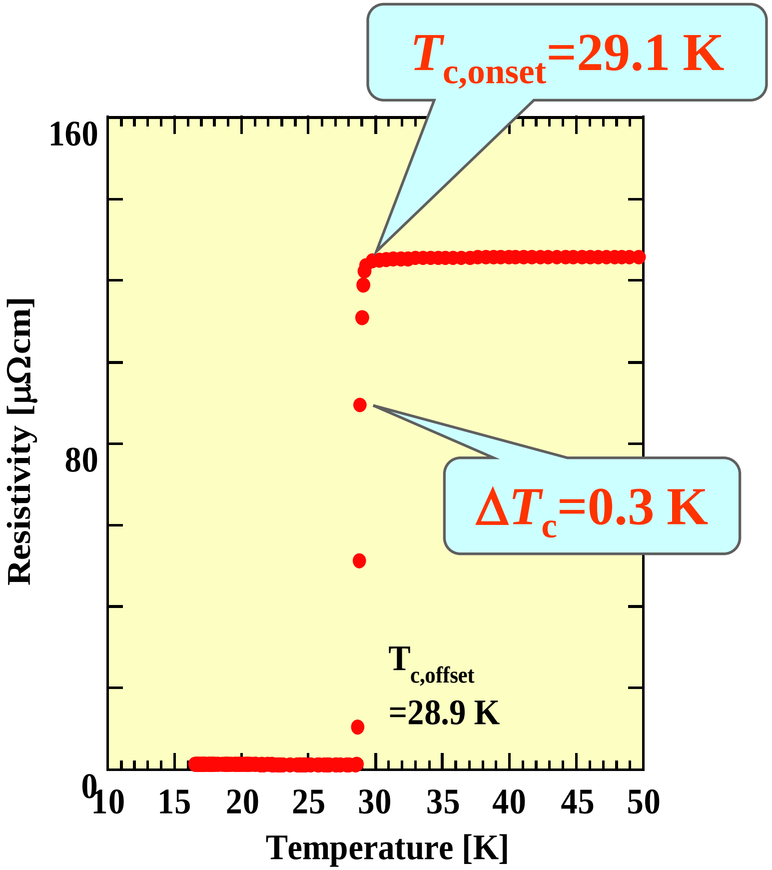
Accomplishment to develop 1.5T magnet at 16th September, 2005.

Hitachi Research Laboratory, Hitachi Ltd.
National Institute for Materials Science

Aoyama-Gakuin University

Recent progress in MgB_2 film (I)

- as-grown MgB_2 film -

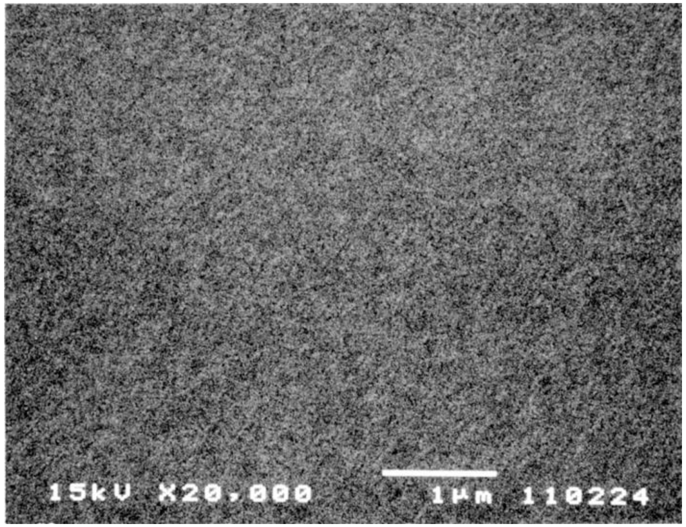


$T_{c,onset}$=29.1 K

ΔT_c=0.3 K

$T_{c,offset}$=28.9 K

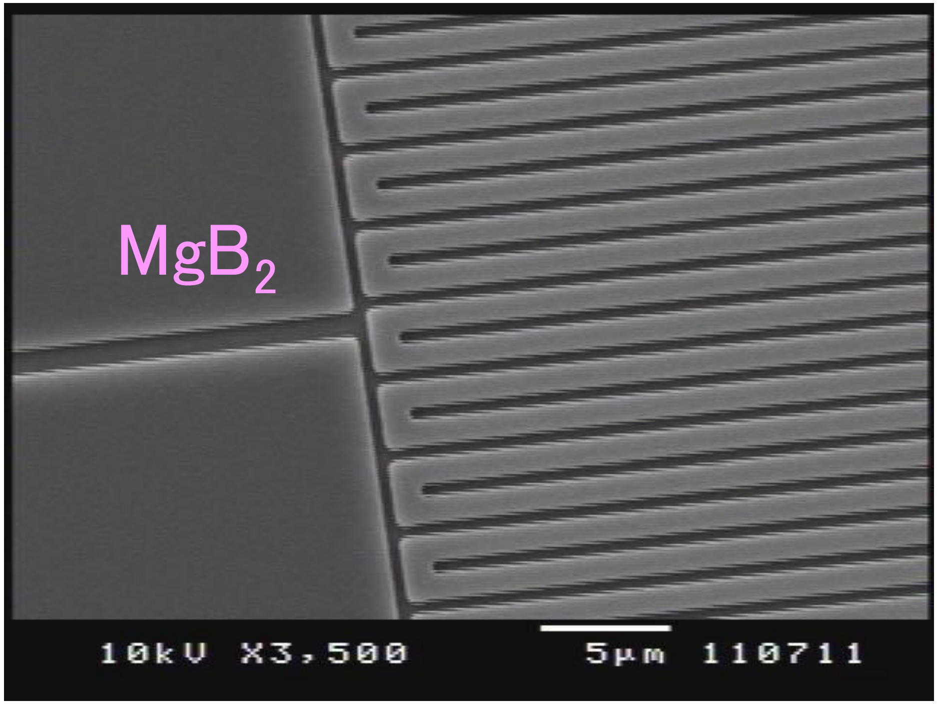
(0001) sapphire substrate
at 250℃

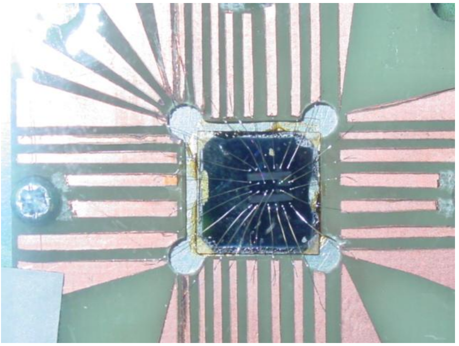


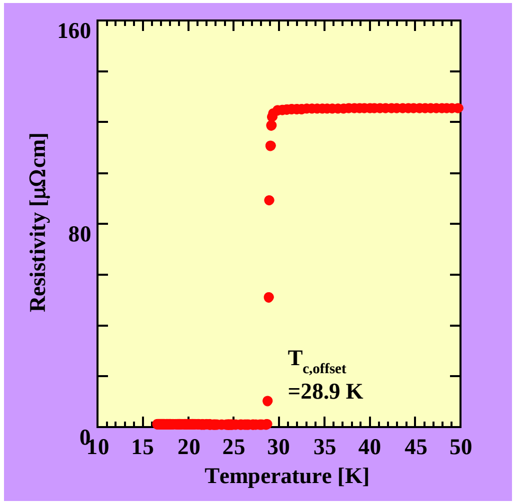
SEM image

Osaka Prefecture University T. Ishida *et al.*

Nano-fabrication of MgB_2



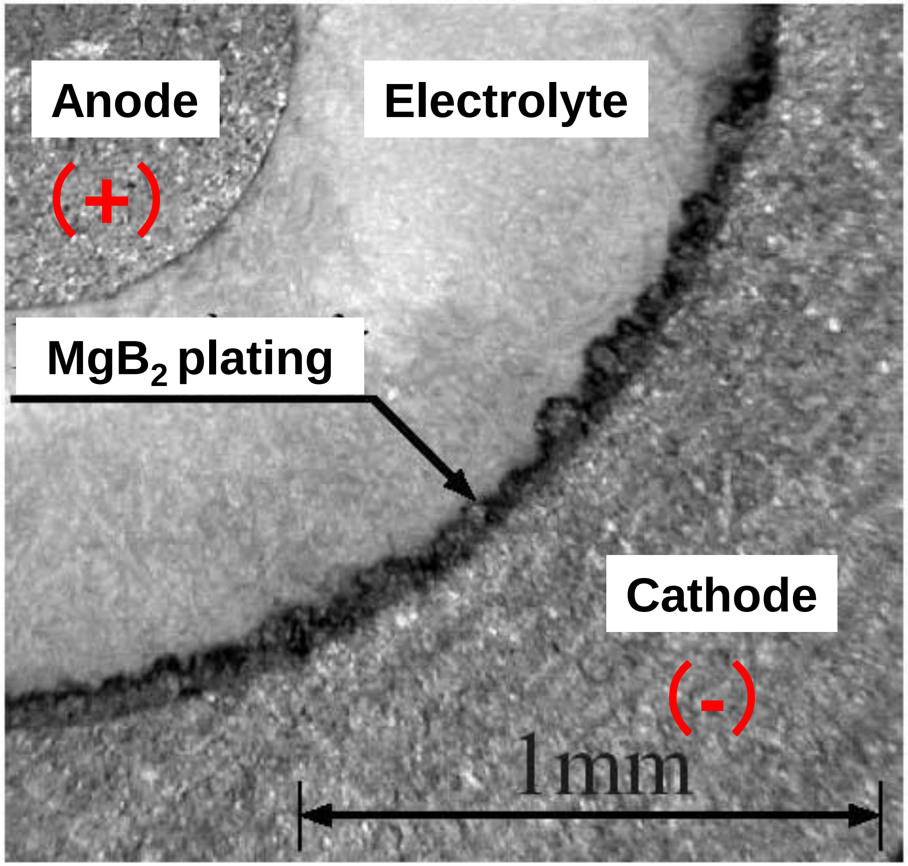




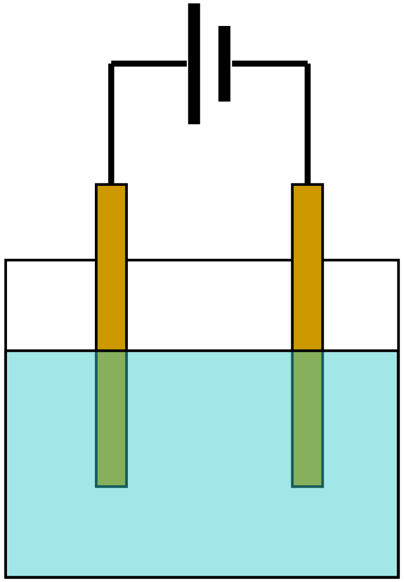
Development toward neutron-detector

Osaka Prefecture University T. Ishida *et al*.

Recent progress in MgB_2 film (II)



SEM image of MgB_2 thin film
fabricated by Galvanization method



A black MgB_2 thin film was successfully synthesized where electrolyte touches a graphite cathode.

National Institute for Materials Science
Japan Atomic Energy Research Institute

H. Abe *et al.*

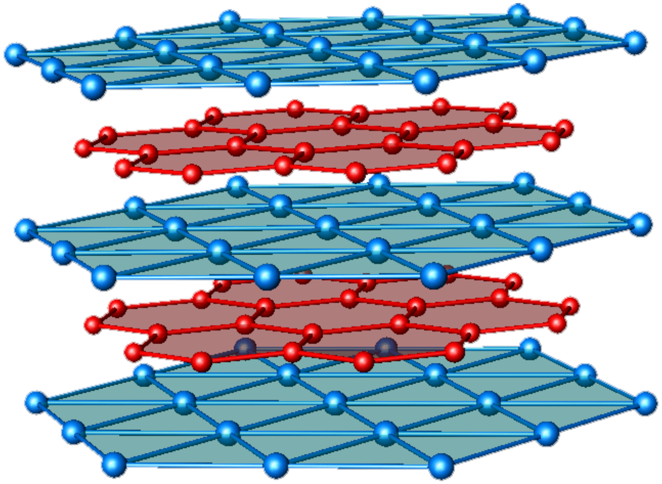
Summary on recent progress in thin film

As a result of homogenization of the electrolyte by mechanical stirring:

	Fe	Stainless steel
T_c (0 T) (K)	37	37
J_c (0 T, 5 K) (A/cm^2)	**$2.3*10^5$**	$2.4*10^4$
J_c (0 T, 20 K) (A/cm^2)	$1.4*10^5$	$7*10^3$
J_c (1 T, 5 K) (A/cm^2)	$1.4*10^5$	$1.3*10^4$

The highest J_c has been achieved in MgB_2 / Fe.

Merits of Application in MgB_2



① Highest-T_c in the intermetallic superconductors

② Starting materials are light and not expensive.

③ Its T_c is a sweet spot for refrigerator.

④ No-weak-link between grains.

⑤ Using cheap sheath-material is feasible.

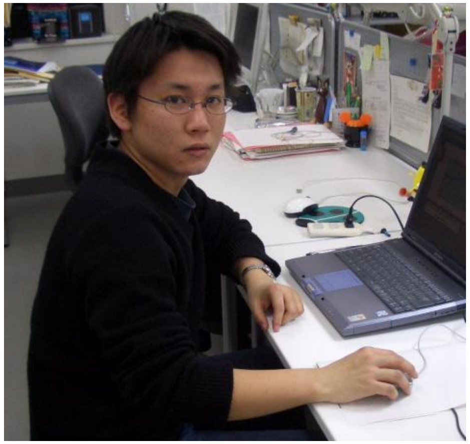
⑥ Heat treatment is unnecessary. or treatment at low temperature and short time is feasible.

⑦ Good performance for bending.

Good cost performance

Superconductivity in Y_2C_3

-Collaborators-



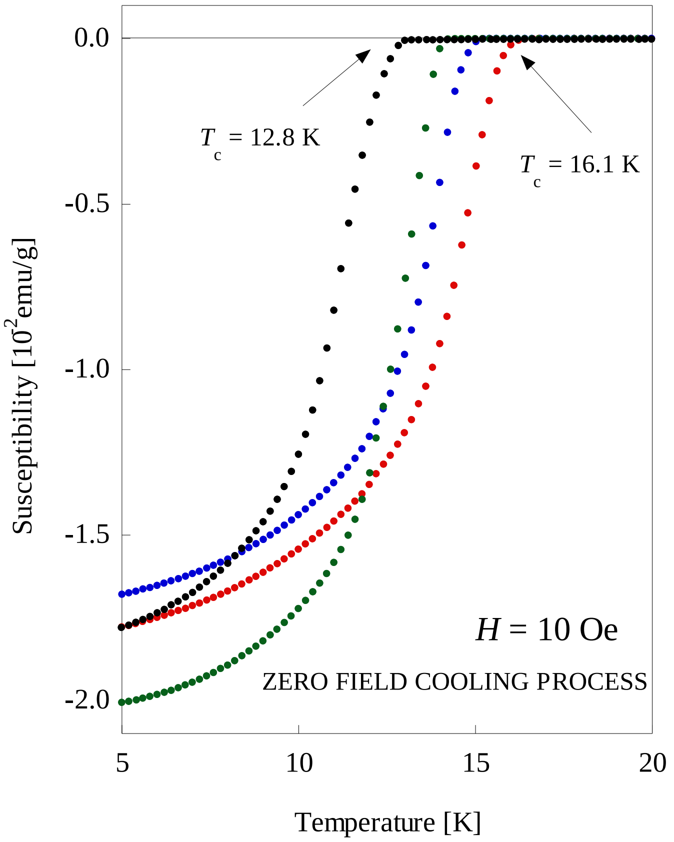
- S. Akutagawa
- MEM/Rietveld analysis
  - K. Osaka, K. Kato and M. Takata (SPring-8)
- Microwave measurement
  - T. Ohashi, H. Kitano, A. Maeda (Univ. of Tokyo)
- NMR
  - A. Harada, H. Mukuda, Y. Kitaoka (Osaka Univ.)

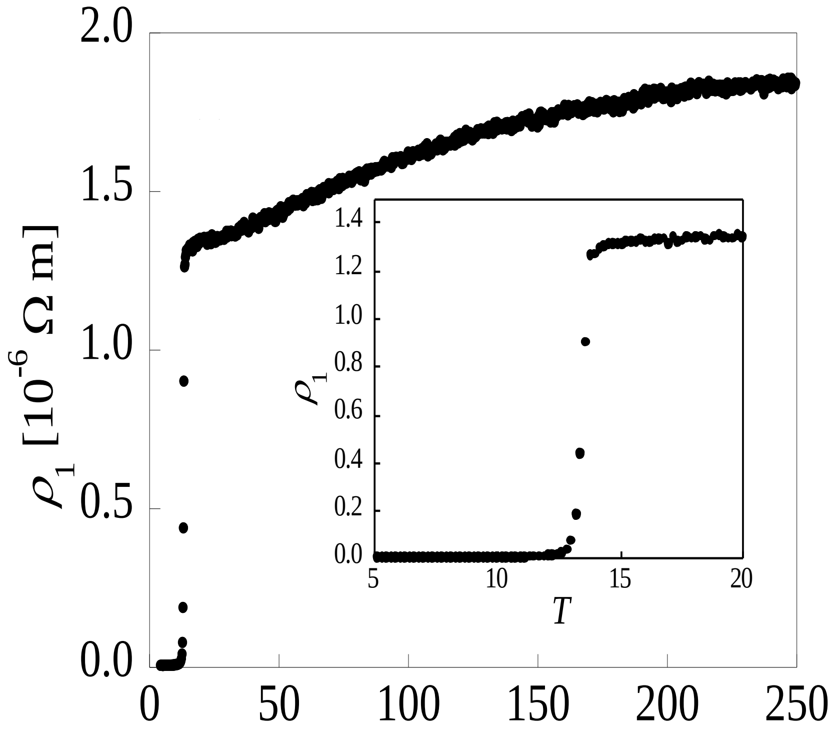
SPring-8

東京大学
THE UNIVERSITY OF TOKYO

大阪大學

Susceptibility & Resistivity of Y_2C_3



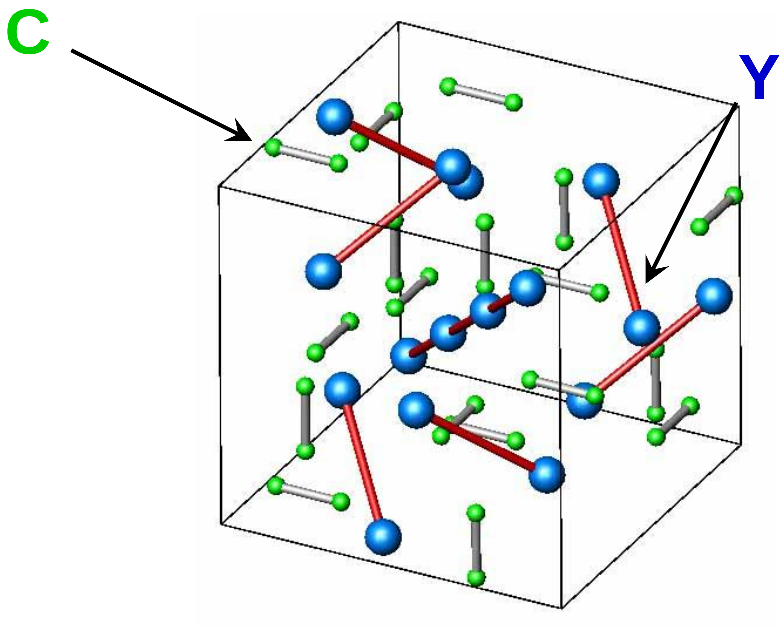


We successfully synthesized high quality Y_2C_3 samples.

T_c is controllable by synthesis condition.

Aoyama-Gakuin
University

Rietveld analysis of Y_2C_3 - high-T_c (18 K)



Structure type : Pu_2C_3 type

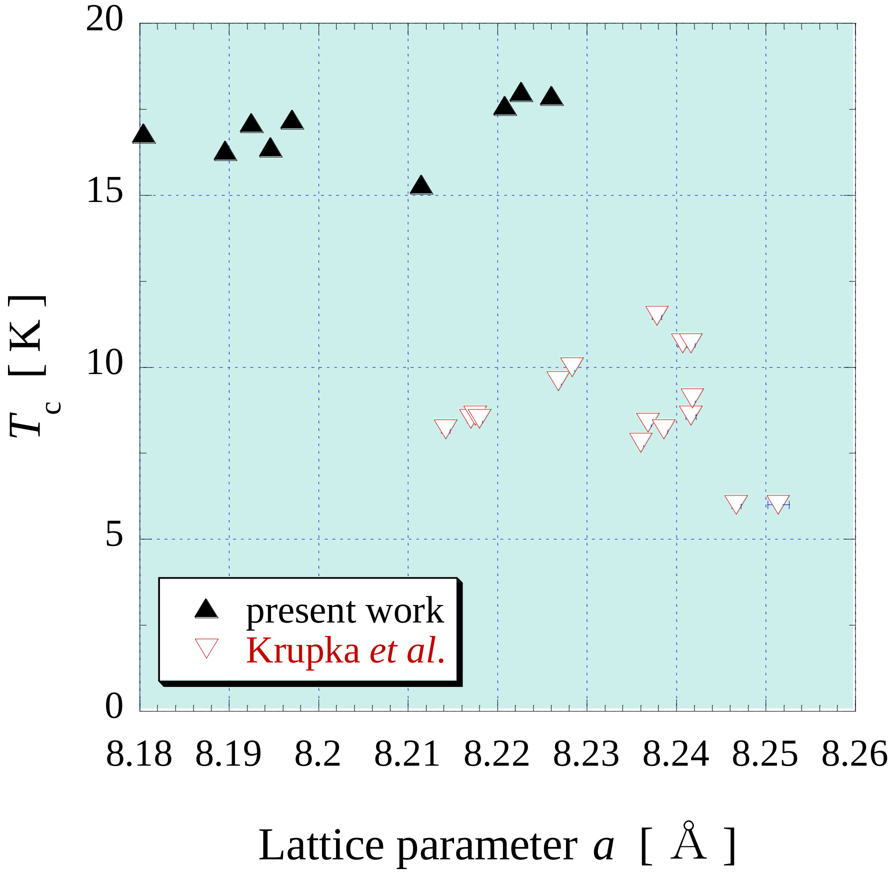
Space group : $I\bar{4}3d$

Y atoms are aligned along the <111> direction and C atoms form dimers.

Crystallographic parameters

a [Å]		8.187099
Y	x	0.049705
	y	0.049705
	z	0.049705
	g	0.995977
	B	0.441354
C	x	0.294788
	y	0
	z	0.25
	g	0.866852
	B	0.937075

Comparison between low-T_c and high-T_c material in Y_2C_3



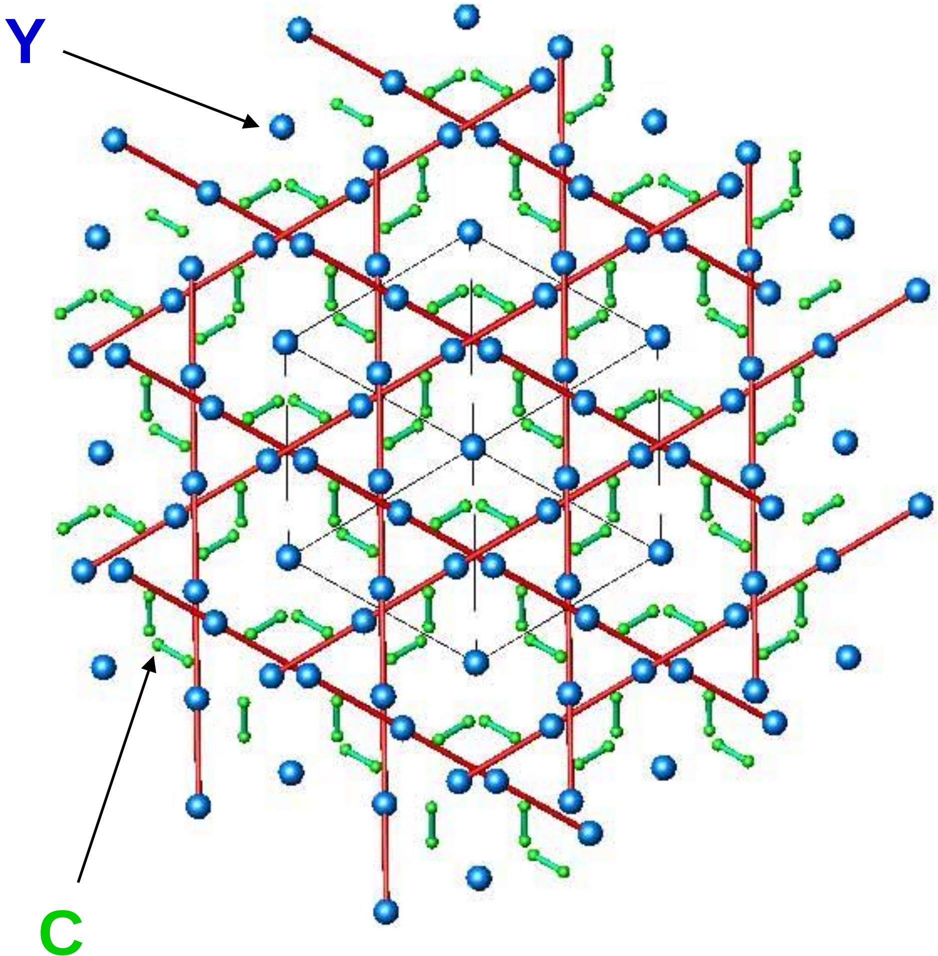
High-T_c material
our work : 8.18~8.23Å

Low-T_c material
Krupka's work : 8.214~8.251Å

The lattice constant, *a*, of high-T_c material is shorter than that of low-T_c material.

Aoyama-Gakuin
University

Refined Structure Parameters



View from [111] direction

High-T_c material

(our work)

$d_{C\text{-}C}$: 1.3134 Å

$d_{Y\text{-}C}$: 2.4876 Å

$d_{Y\text{-}Y}$: 3.5451 Å

Low-T_c material

(V.I. Novokshonov *et al*.)

$d_{C\text{-}C}$: 1.5298 Å

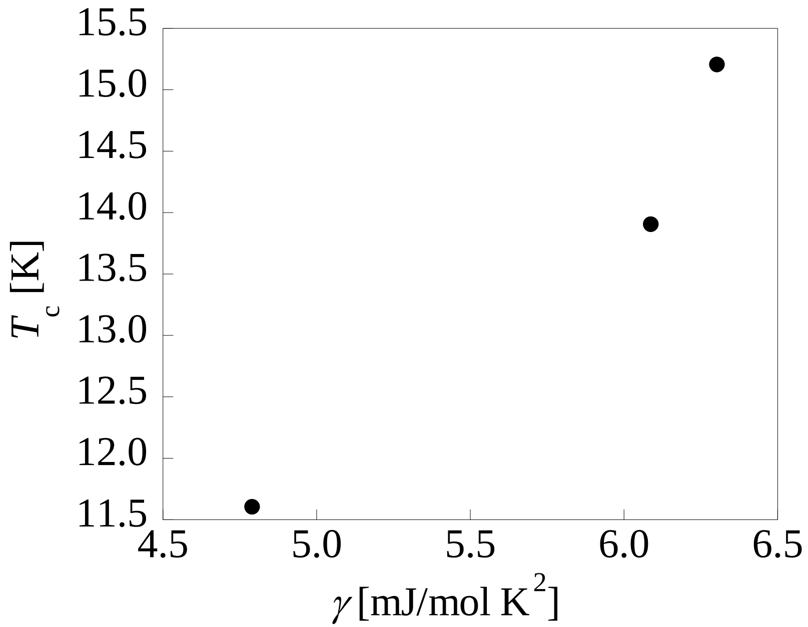
$d_{Y\text{-}C}$: 2.556 Å

$d_{Y\text{-}Y}$: 3.5652 Å

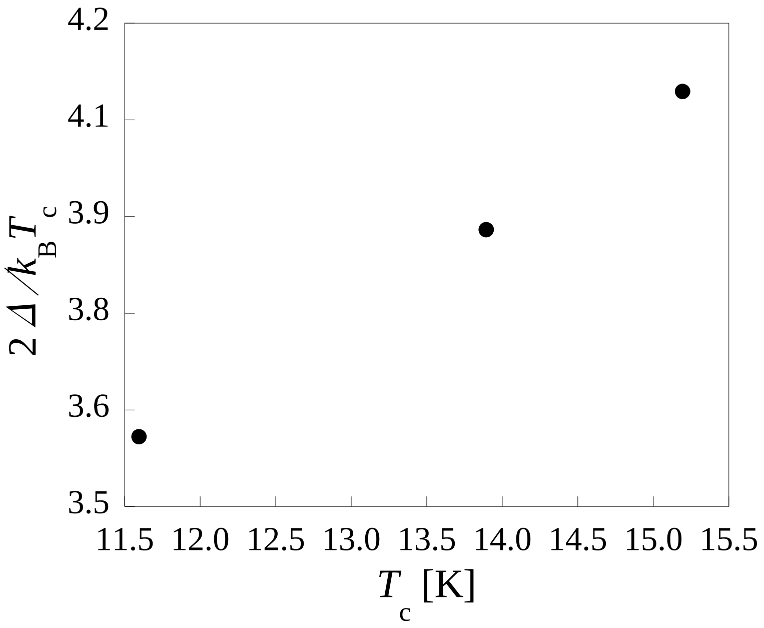
C-C distance of high-T_c material is shorter than that of low-T_c material.

Macroscopic parameters

T_c vs. γ



T_c vs. $2\Delta_0/k_BT_c$



T_c depends on γ.

$2\Delta_0/k_BT_c$ increases with increasing T_c.

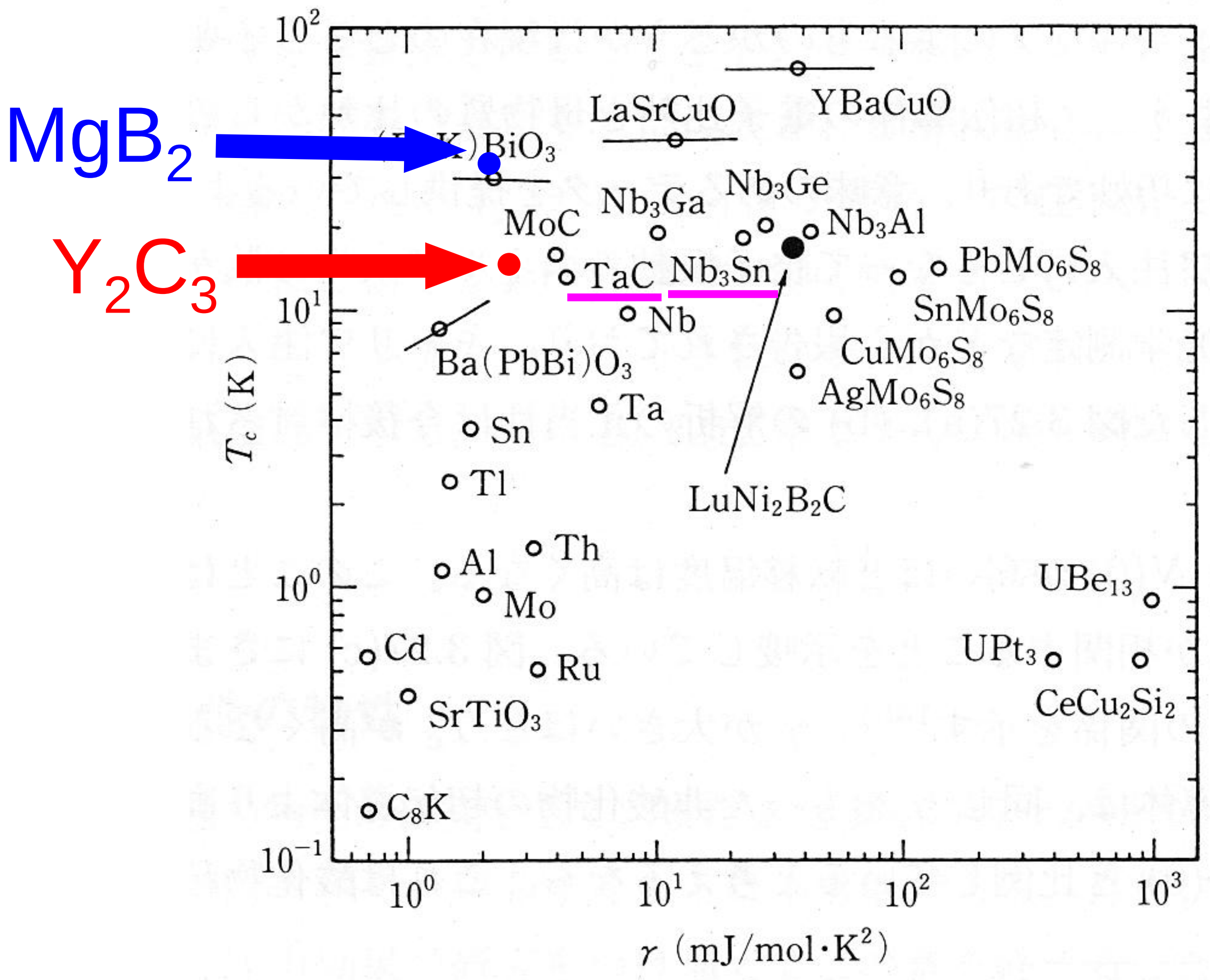
Sommerfeld constant : $\gamma = \pi^2 k_B^2 D(E_F)/3$

Aoyama-Gakuin University

Various parameters of Y_2C_3
Comparison with various T_c phases

T_c (K)	11.6	13.9	15.2
© (mJ/mol·K^2)	4.7	6.0	6.3
θ_D (K)	540	530	530
$\mu_0 H_{c2}(0)$ (T)	22.7	24.7	26.8
$2\Delta/k_B T_c$	3.6	3.9	4.1

Relationship between γ and T_c



MgB_2

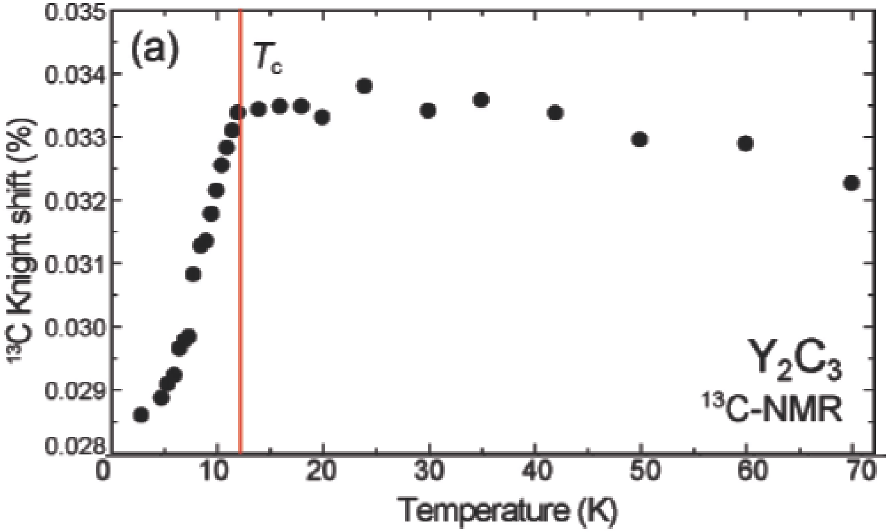
Y_2C_3

^{13}C NMR Knight shift : singlet or triplet?

Temperature dependence of Knight shift

Knight shift is decreased below T_c.

→ **Spin singlet**



A. Harada et al., J. Phys. Soc. Jpn. **76(2)** (2007) 023704/1-4.

^{13}C NMR $1/T_1$: Two-gap superconductor ?

$T_1T \propto 1/N(E)$

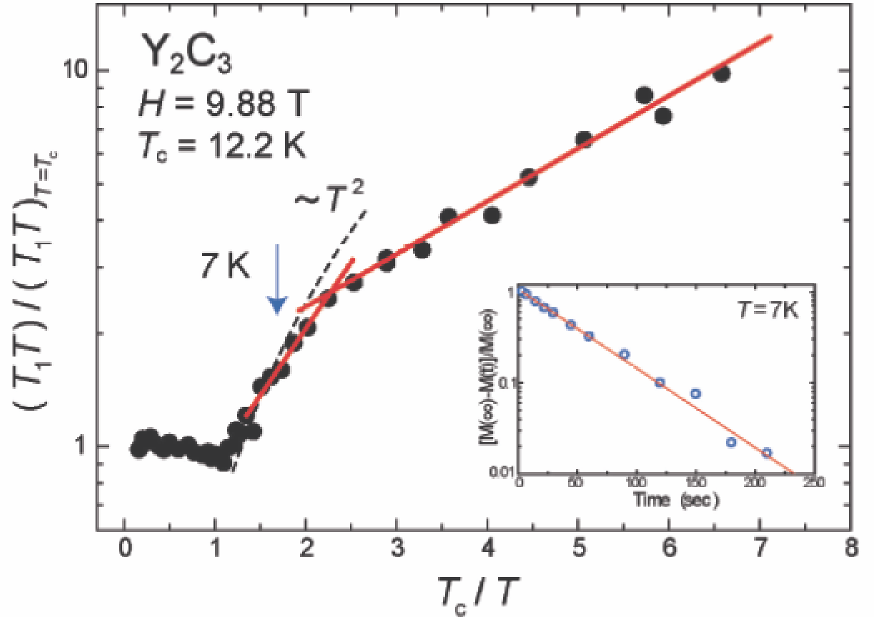
$1/T$

We observed ***two*** *components in 1/T dependence.*

Two isotropic gaps exit in Y_2C_3.

Large gap: $2\Delta_\alpha/K_BT_c = 5$ ($\alpha = 0.75$)

Small gap: $2\Delta_\beta/K_BT_c = 2$ ($\beta = 0.25$)



Dotted line shows $\sim T^2$ (line node).

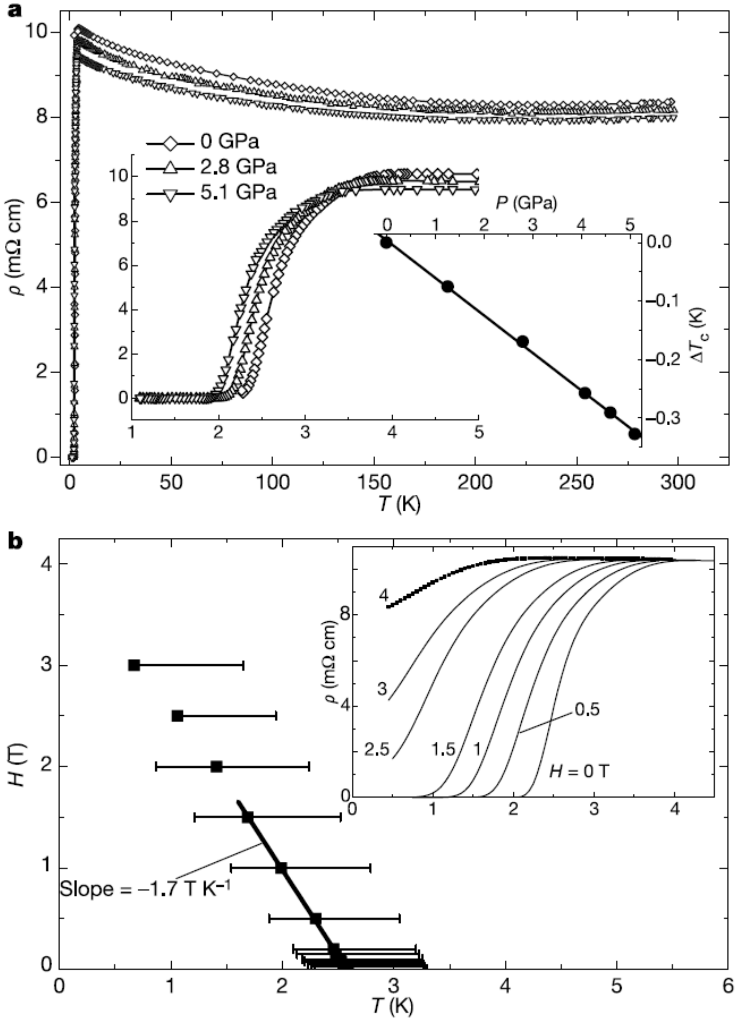
The inset shows a simple exponential recovery curve of nuclear magnetizatio

A. Harada et al., J. Phys. Soc. Jpn. **76(2)** (2007) 023704/1-4.

Aoyama-Gakuin University

Superconductivity in B-doped Diamond

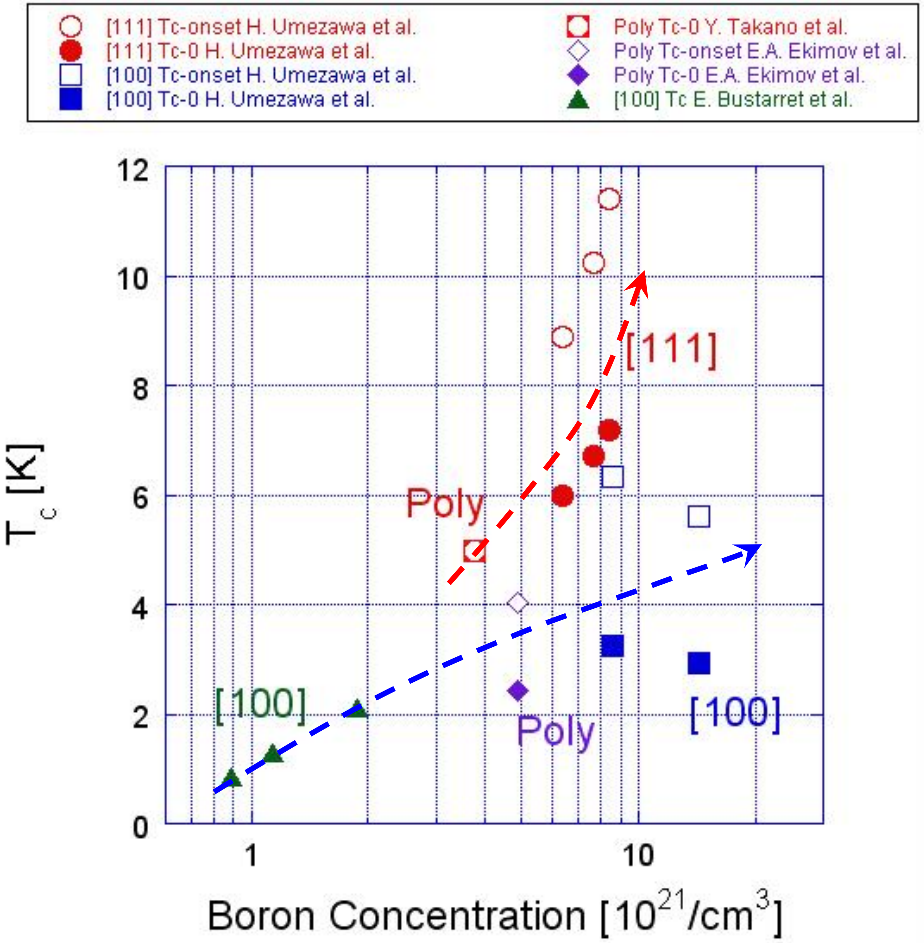
- $T_c \sim 4K$, $H_{c2} \sim 3.5T$
  - Type-II SC
- Synthesis at 8-9GPa, 2500-2800K
- B concentration
  - 4-5x10^{21} /cm^3



E.A.Ekimov *et al.*, Nature 428, 542(2004)

Difference of T_c between (100) & (111) films grown by CVD method

- At same B-concentration : about $8.5 \times 10^{21} \mathrm{cm}^{-3}$
  - (111)
    - T_c onset = 11.5K
    - T_c zero = 7.4K
  - (100)
    - T_c onset = 6.3K
    - T_c zero = 3.2K



Superconductivity in B-doped Diamond

-Collaborators-

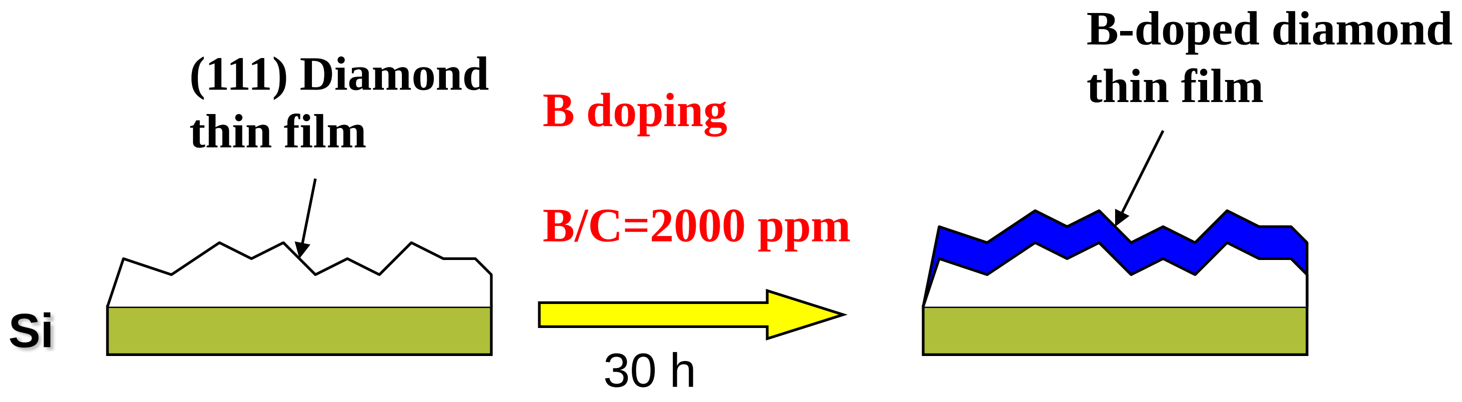
- T. Muranaka

- Preparation of Diamond films
  - K. Kobashi (Electronics & Infomation Technology Laboratory, Kobe Steel Ltd.)

KOBELCO
神戸製鋼

Superconductivity in B-doped diamond

Polycrystalline film



(111) Diamond thin film

Si

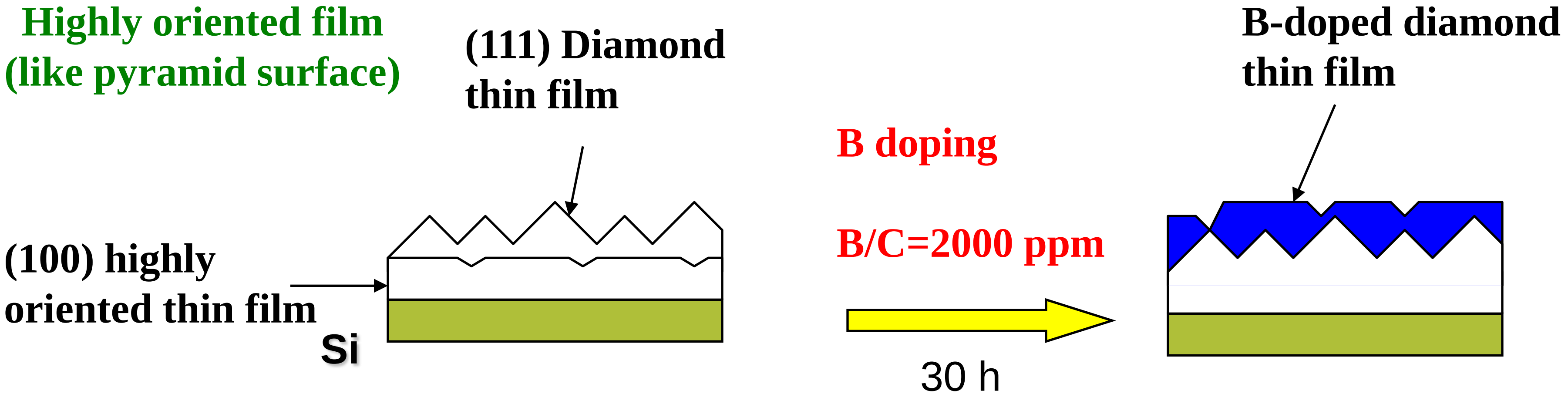
B doping

B/C=2000 ppm

30 h

B-doped diamond thin film

Highly oriented film (like pyramid surface)



(111) Diamond thin film

(100) highly oriented thin film

Si

B doping

B/C=2000 ppm

30 h

B-doped diamond thin film

(100) surface is appeared by B-doping.

Aoyama-Gakuin University

SEM images of diamond thin film

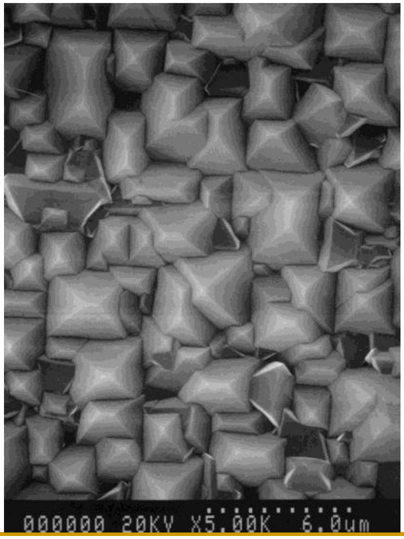
Polycrystalline thin film

B-doping

B/C=2000 ppm

30 h

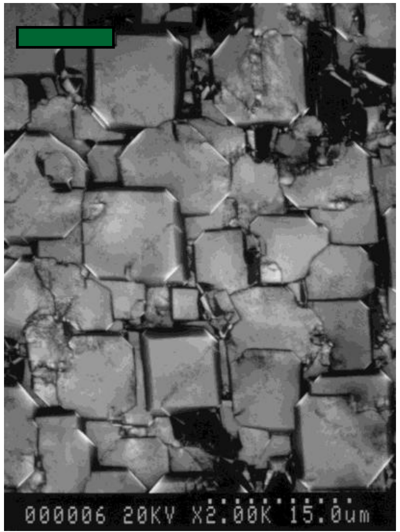
Highly oriented thin film (like pyramid surface)



B-doping

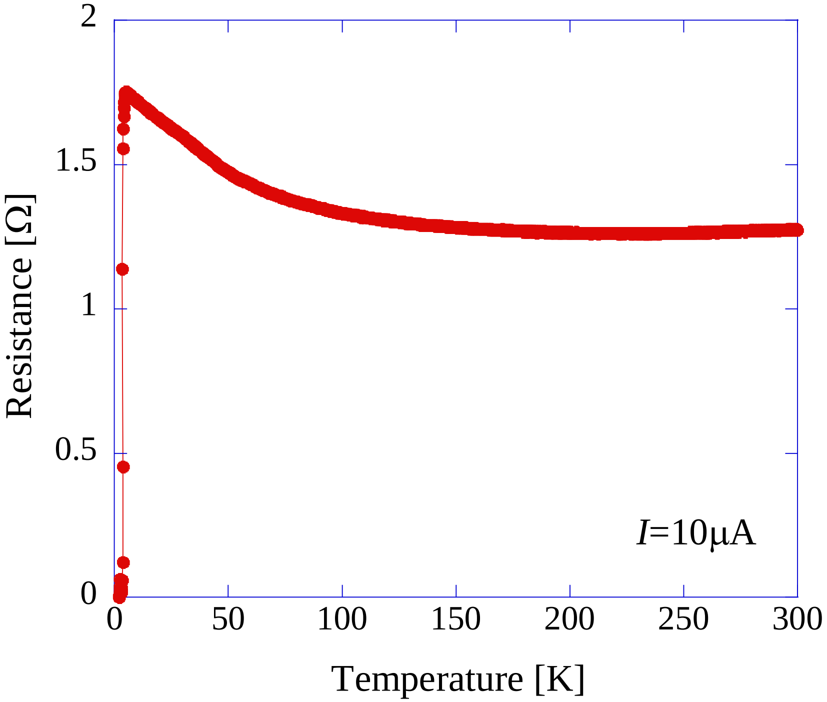
B/C=2000 ppm

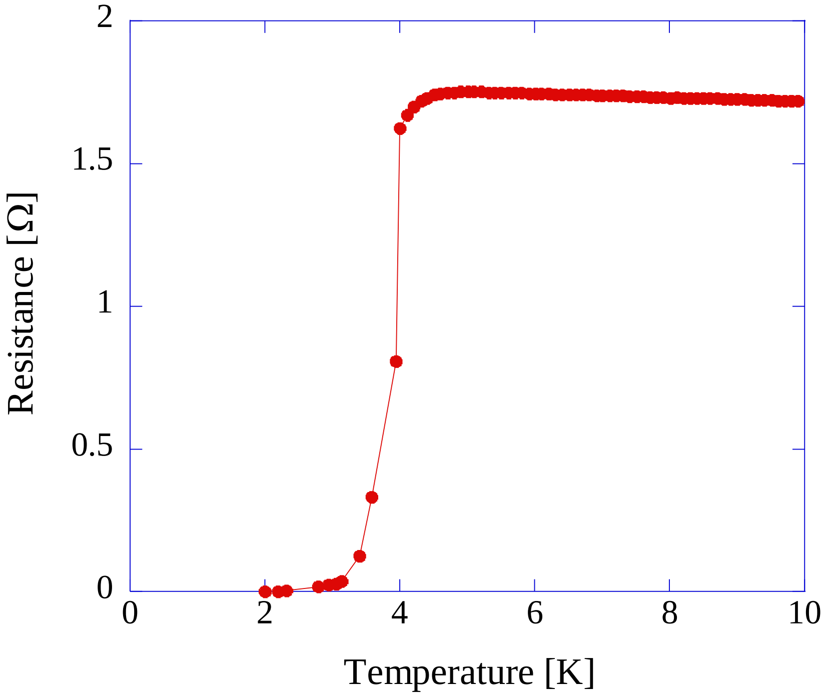
30 h



(100) surface is appeared by B-doping.

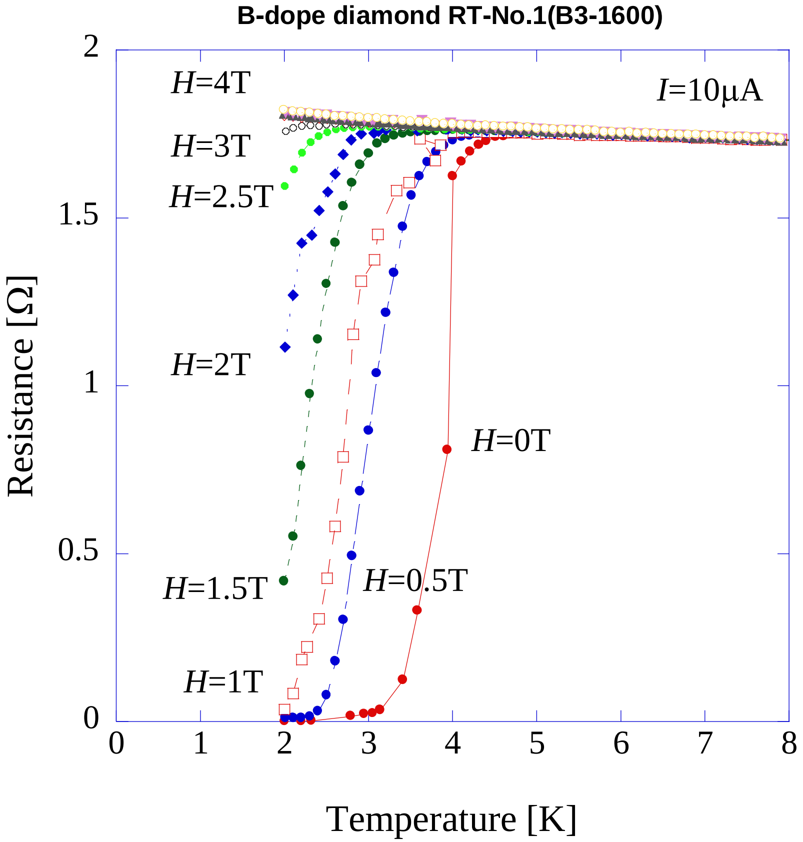
Resistance in B-doped diamond on highly oriented diamond thin film

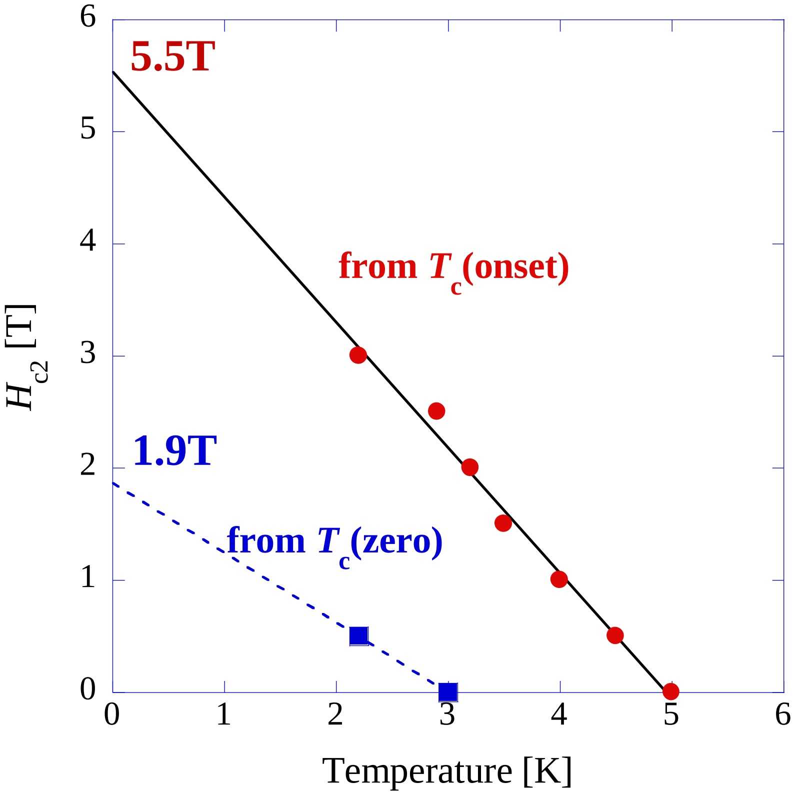




- **T_c(onset)=5.0K & T_c(zero)=3.0K**

Resistance in a magnetic field & H_{c2} in B-doped diamond on highly oriented diamond thin film



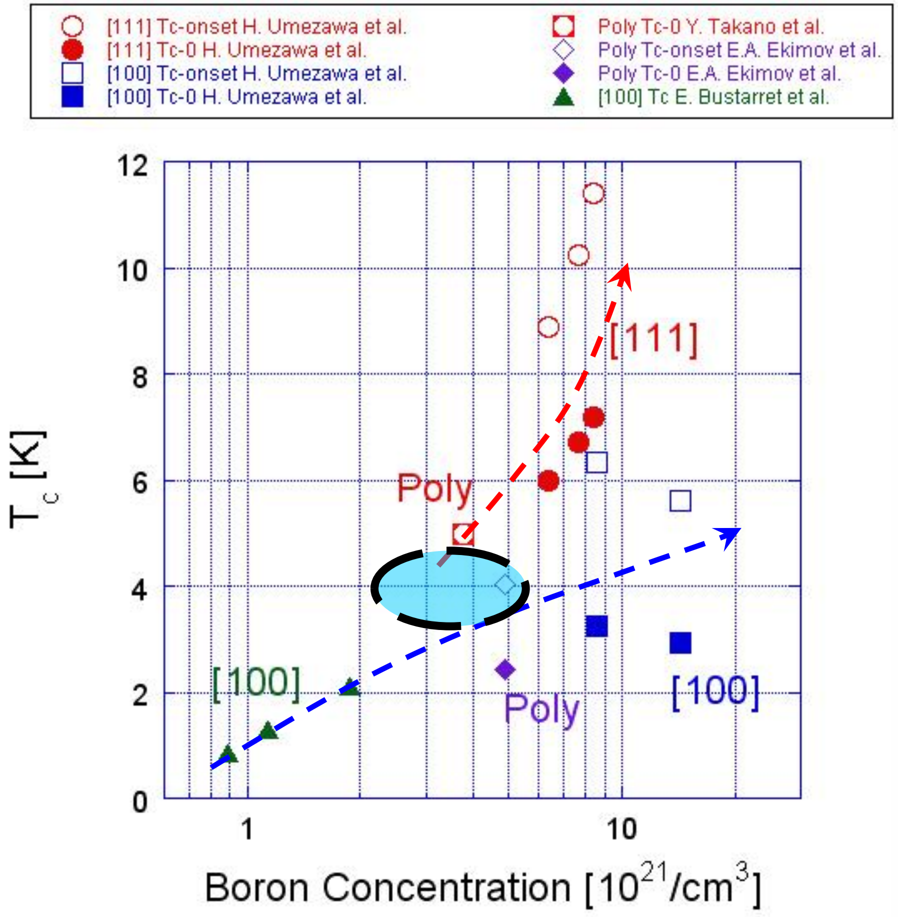


- **H_{c2}(inset) & H_{c2}(zero) are estimated to be about 5.5T &1.9T.**

Aoyama-Gakuin University

Phase diagram for T_c and B-concentration

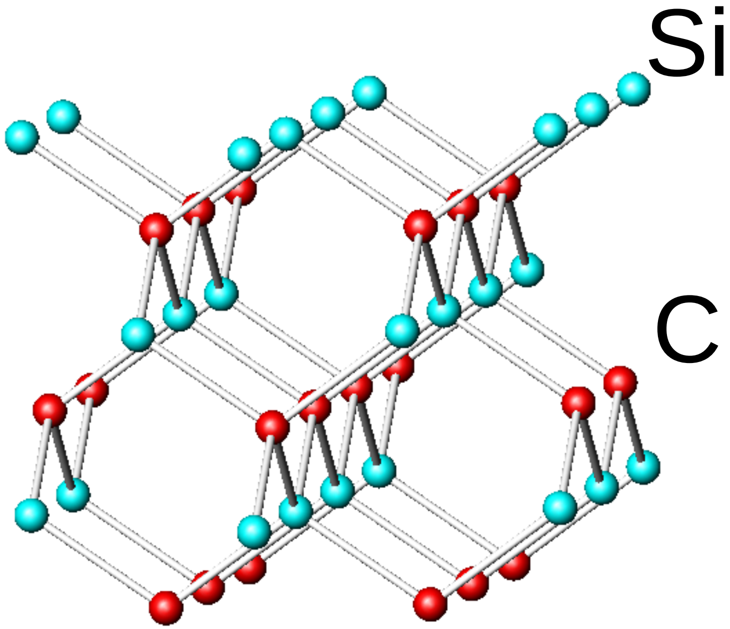
- Boron concentration of our samples are estimated to be about $2\text{-}5\times10^{21}/\mathrm{cm}^3$.
  - Relatively under-doping region
- We will be synthesizing by new method & condition.
  - Chasing for higher-T_c



Superconductivity in B-doped SiC -Collaborators-

- Z.-A. Ren, J. Kato, T. Muranaka
- AC susceptibility
  - M. Kriener, Y. Maeno (Kyoto Univ.)

Searching for new superconductivity in a wide gap semiconductor with a diamond lattice structure



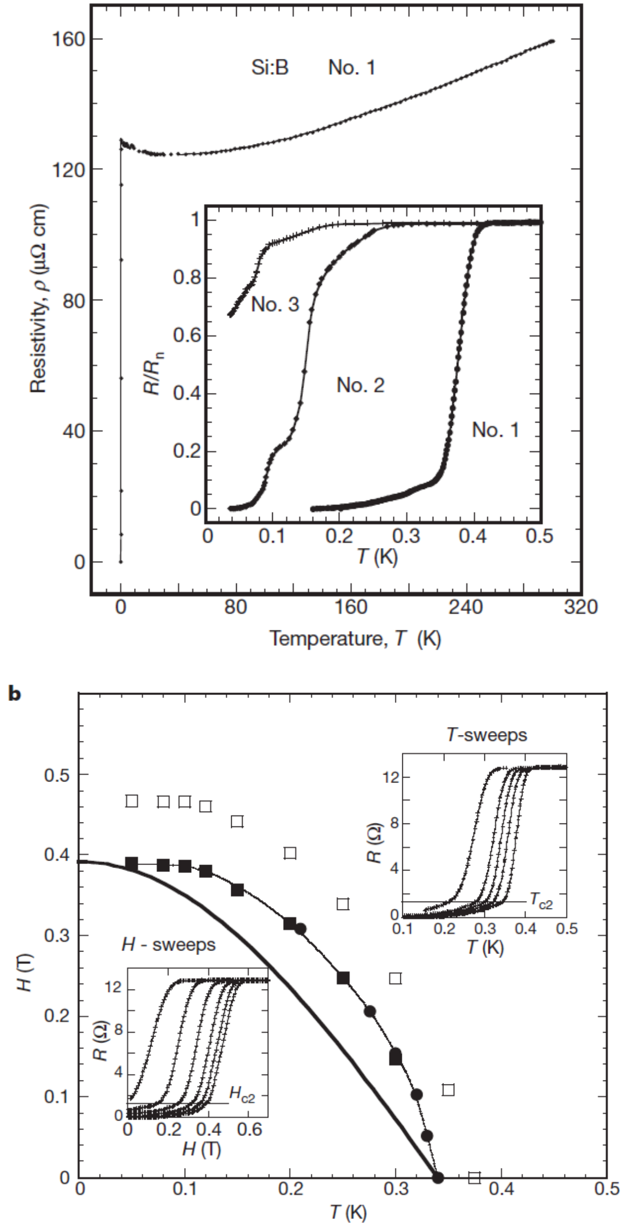
Crystal structure of 3C-SiC

- We try to dope B atom for carrier doping.

Background

Superconductivity in B-doped Si

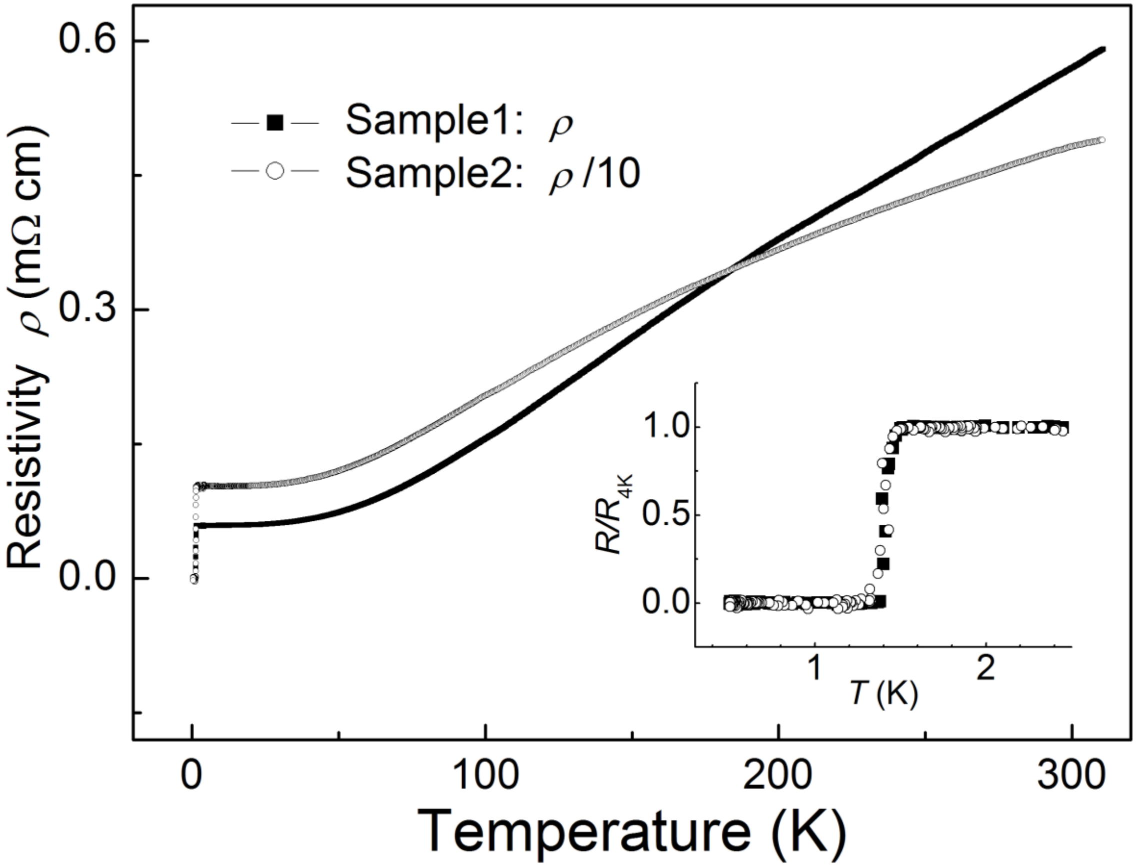
- B-doping to Si by UV laser
- $T_c \sim 0.35$K, $H_{c2} \sim 0.4$T
  - Type-II SC
- Carrier (hole) density
  - $\sim 5 \pm 2 \times 10^{21}$ cm^{-3}



E. Bustarret *et al*., Nature 444, 465 (2006).

Aoyama-Gakuin
University

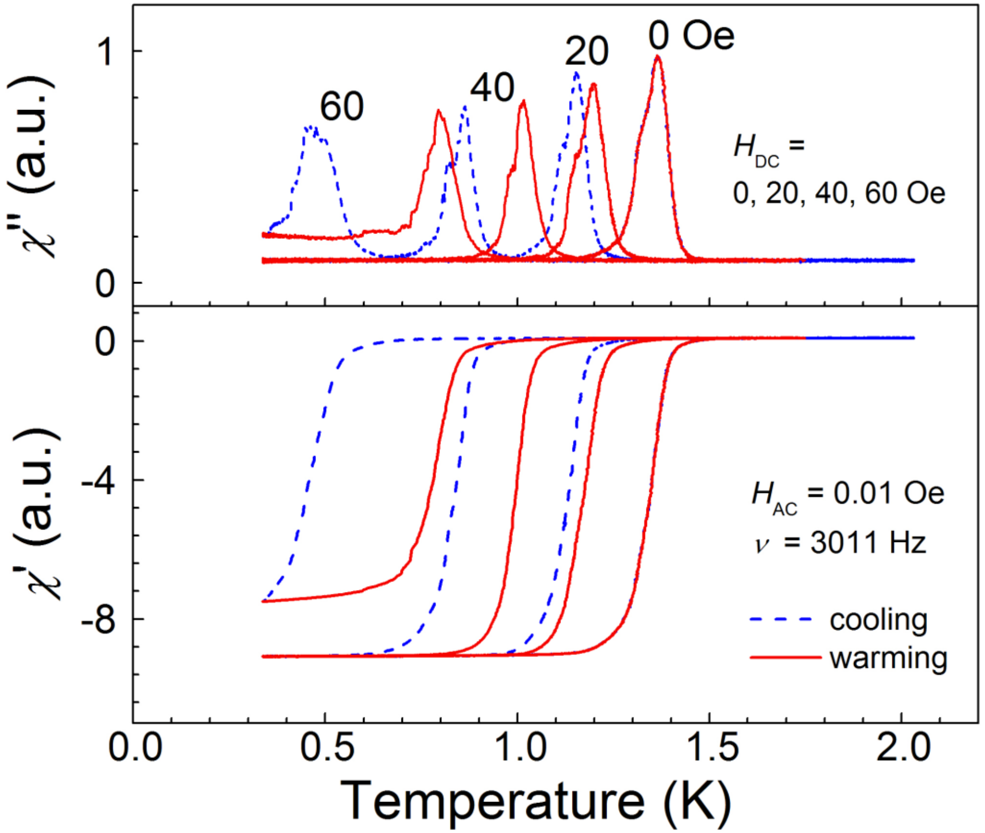
Temperature dependence of resistivity



- Superconductivity was observed at T_c=1.4 K

Aoyama-Gakuin
University

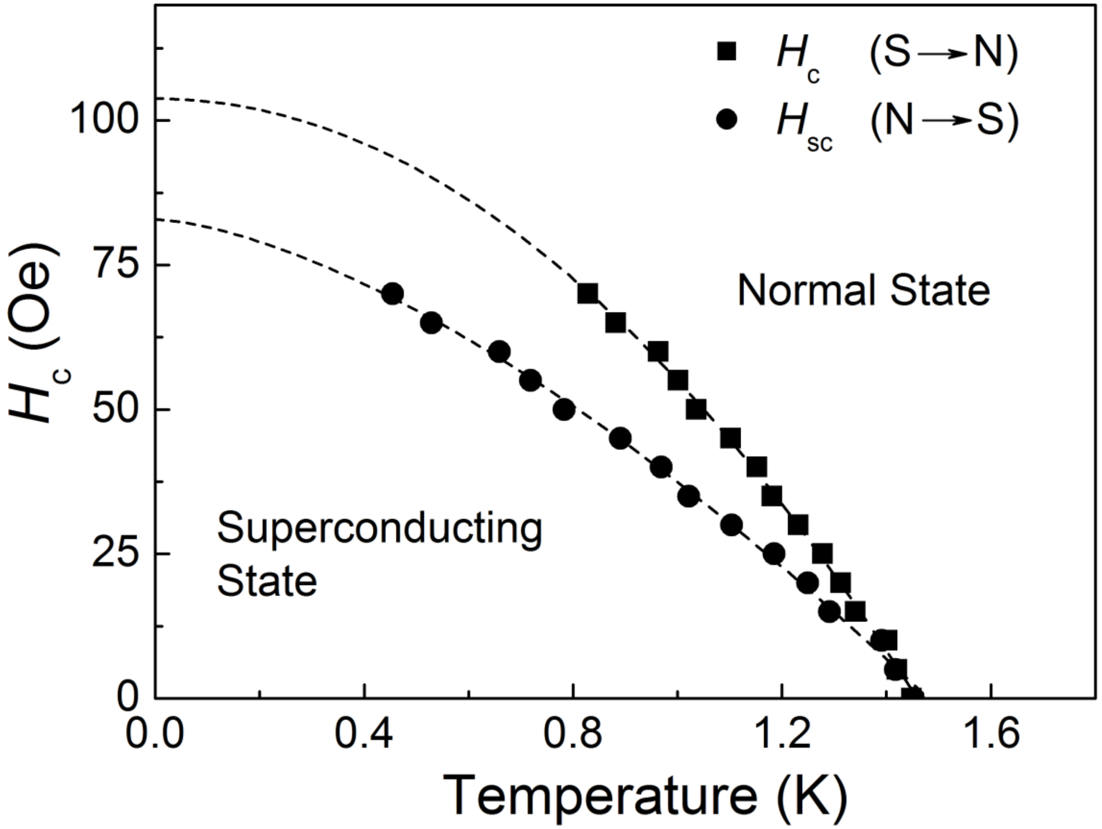
Temperature dependence of AC susceptibility



- We observed the in-field hysteresis and the absence of a hysteresis in zero field.
  - Strong evidence for **type-I superconductivity**.

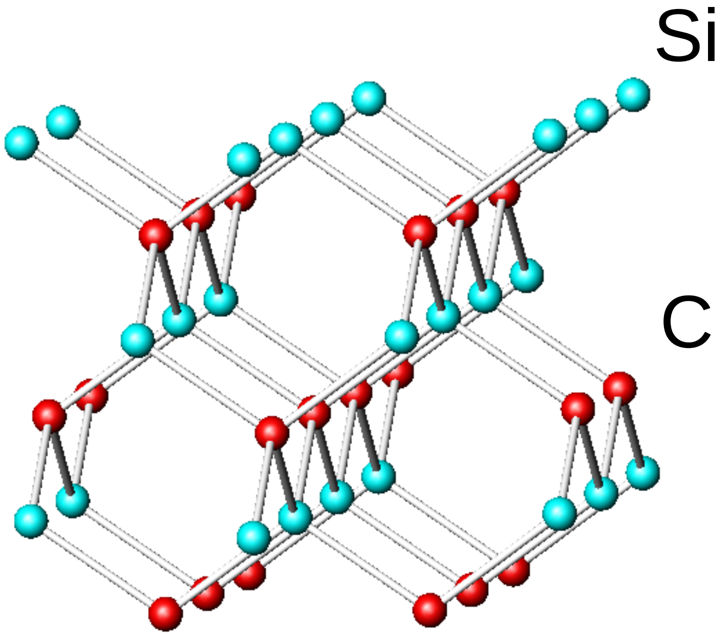
Aoyama-Gakuin University

H-*T* phase diagram

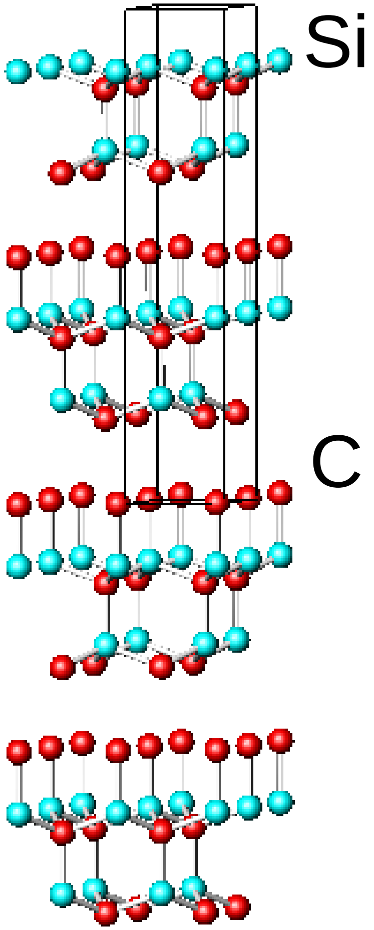


- We determined $H_{sc}(0)$ to be (83±5) Oe
  - GL parameter $\kappa \leq 0.34$ (type-I)

Problem in superconductivity in B-doped SiC



OR



Crystal structure of 3C-SiC

Crystal structure of 6H-SiC

Many approaches to higher-T_c superconductors

1) Carrier-doped CuO_2 planes

- Unidentified Superconducting Objects –
- Extremely large energy gap observed by STM -

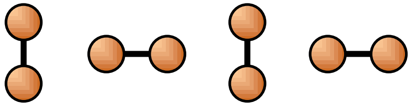
2) Cu-oxides having a different crystal structure

- Ladders -
- Lieb model - etc…

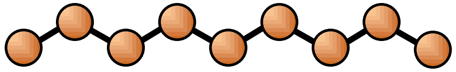
3) Metal superconductors including light elements (boron, carbon etc…)

4) **Carrier-doped clusters / nanotubes**

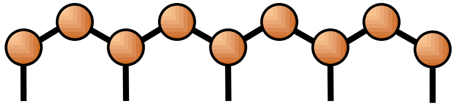
Network of elements in Boride, Carbide and Silicide compounds



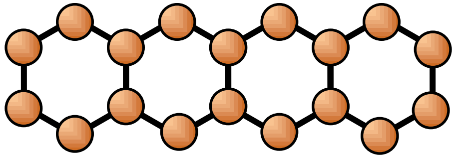
pairs



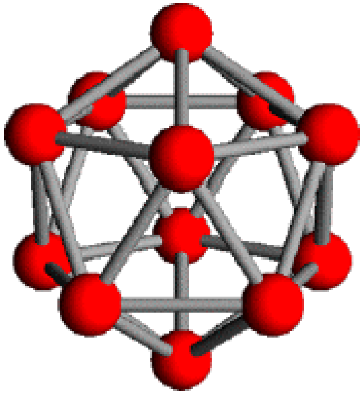
zigzag chains



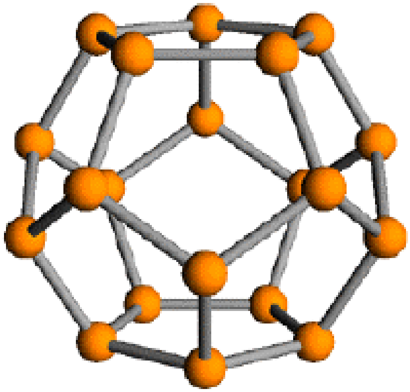
branched chains



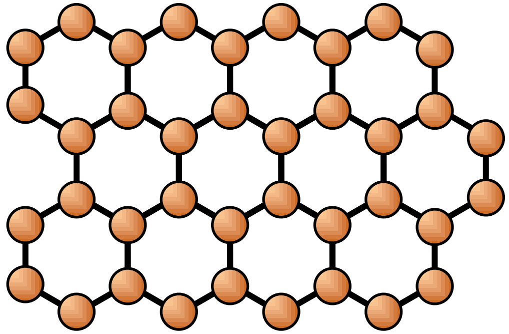
double chains



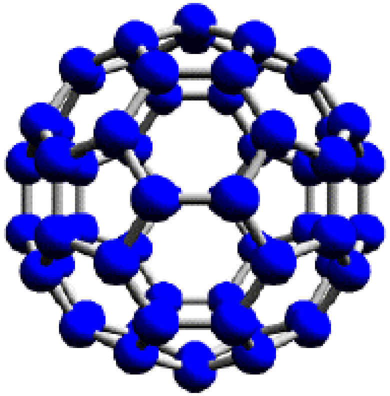
B_{12} cluster



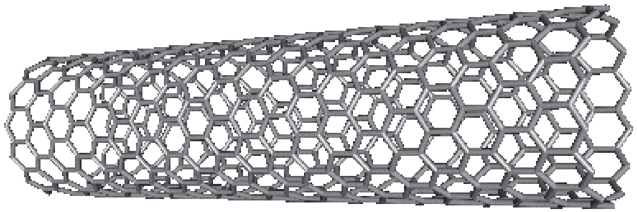
Si_{20} cluster



two-dimensional network

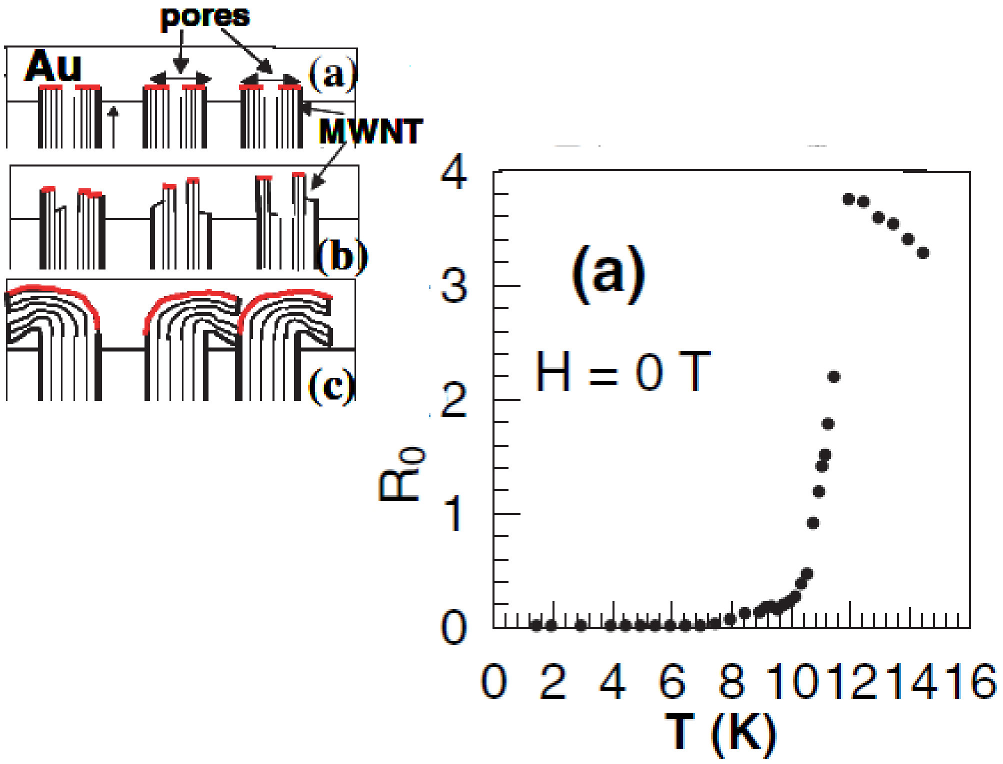


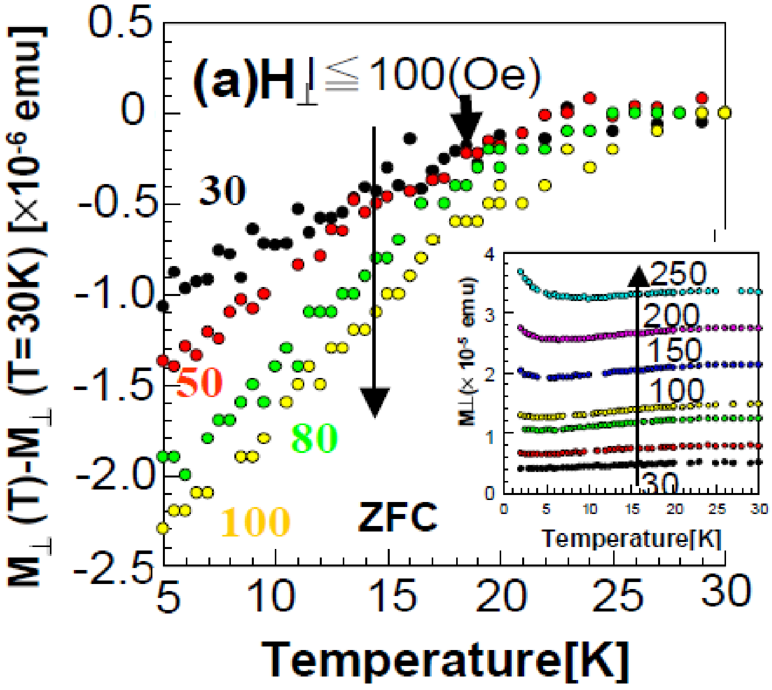
C_{60} cluster



Carbon nanotube

Superconducting signal in end-bonded multiwalled carbon nanotubes





I. Takesue et al.,Phys. Rev. Lett. 96, 057001 (2006).

N. Murata et al., cond-mat/0703599.

Aoyama-Gakuin University

Clathrate-type silver-oxide: Ag_6O_8MX superconductor

-Collaborators-

- K. Kawashima and M. Ishii

  (Aoyama Gakuin Univ.)

- M. Kriener, H. Takatsu, S. Yonezawa and Y.Maeno

  (Univ. of Kyoto)

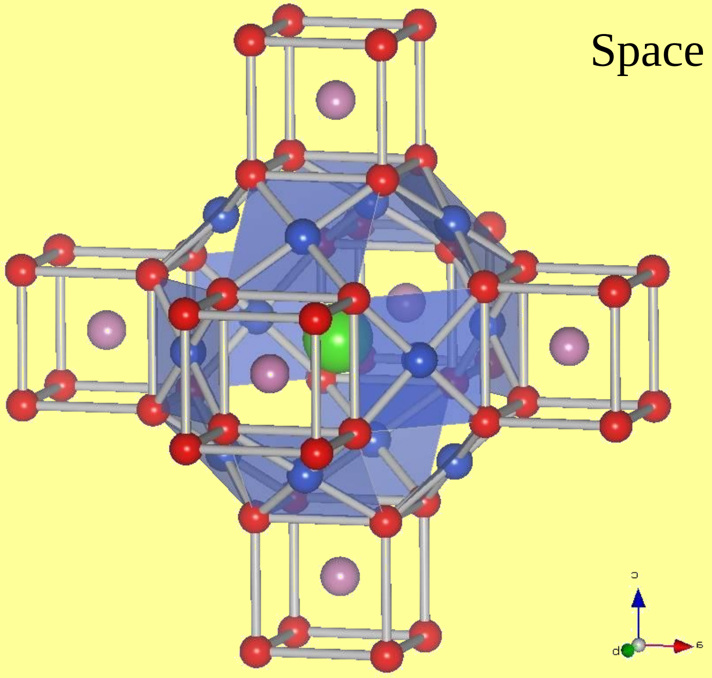
Crystal structure of Ag_6O_8MX

The silver-oxide Ag_6O_8MX (M = cation, X = anion) has a clathrate-type structure which consists of face sharing Ag_6O_8 cage containing anion (X^-) at its center.

- $Ag_6O_8AgNO_3$ (T_c=1.04 K)
- $Ag_6O_8AgBF_4$ (T_c=0.35 K)
- $Ag_6O_8AgHF_2$ (T_c=0.15~1.5 K)
- $Ag_6O_8AgHSO_4$
- $Ag_6O_8AgHCO_3$
- $Ag_6O_8AgClO_4$

Crystal system: Cubic

Space group: *Fm3m*



● O

● Ag(II, III)

● cation(M^+)

● anion (X^-)

[1] J. Selbin *et al*., J. Inorg. Nucl. Chem., **20** (1961) 91.
[2] M. B. Robin *et al*., Phys. Rev. Lett. **17** (1966) 917.
[3] M. Jansen *et al*., J. Alloys and Compounds **183** (1992) 45.

In a previous repot

ex. $Ag_6O_8AgNO_3$

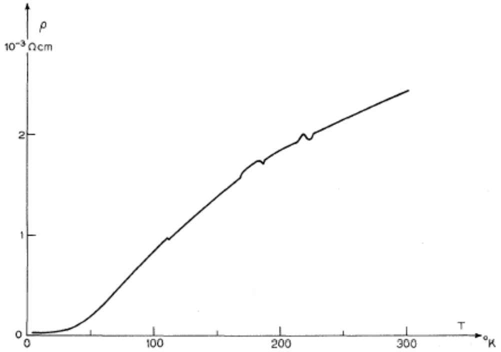
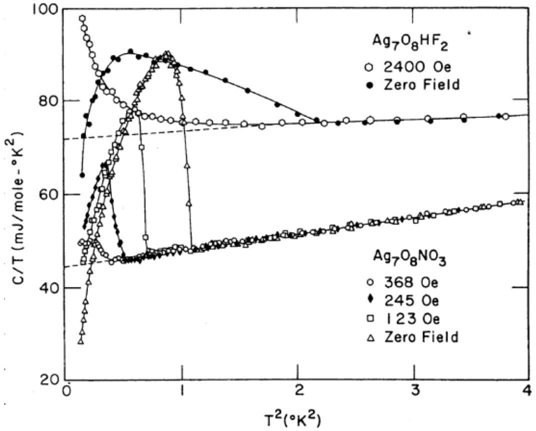


FIG. 1. The temperature-resistivity curve for a single crystal of $Ag_7O_8NO_3$.

$Ag_6O_8AgNO_3$ shows multi phase-transitions with decreasing temperature.

Robin and co-workers suggested that these transitions were generated with the structural-phase transitions.

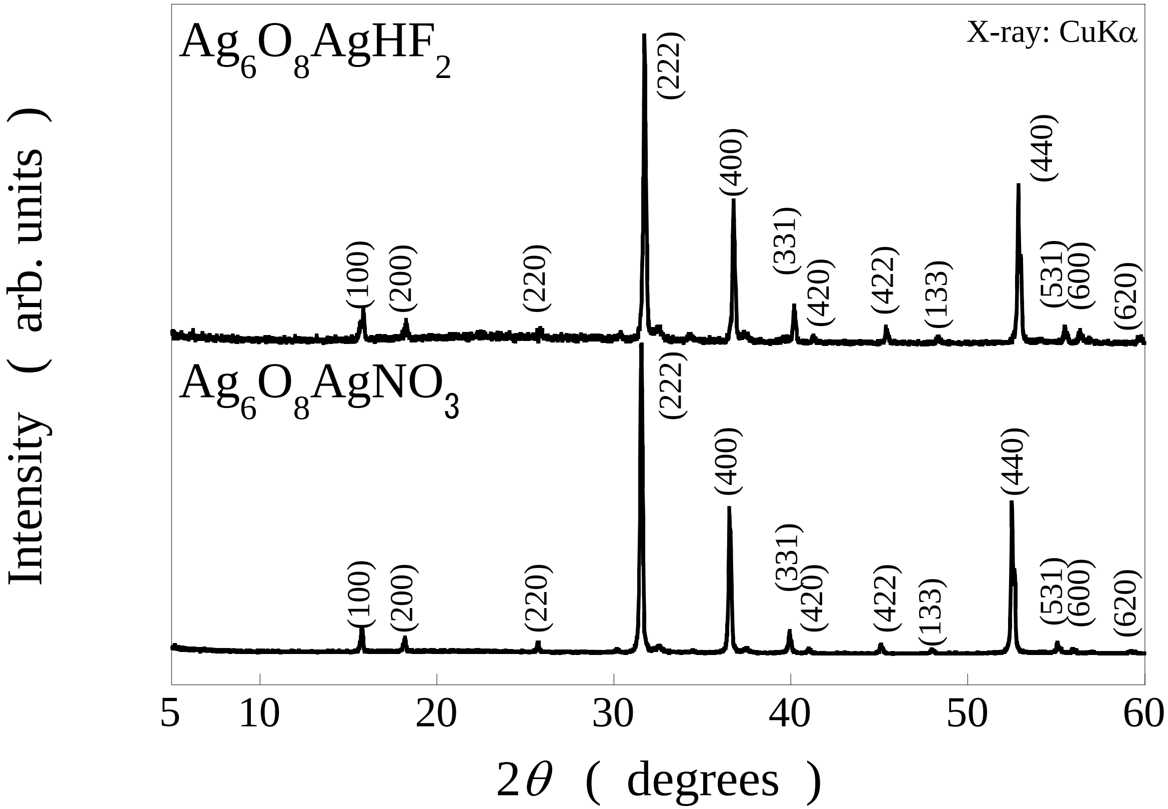


$Ag_6O_8AgNO_3$ shows superconductivity at 1.04 K

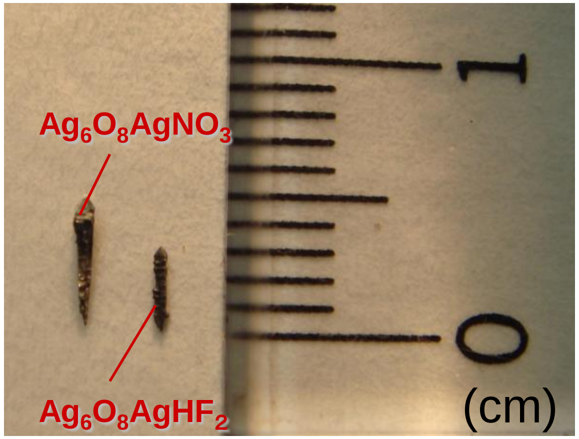
[4] M. B. Robin *et al*., Phys. Rev. Lett. **17** (1966) 917.

[5] M. M. Conway et al,. J. Phys. Chem. Sol. **31** (1970) 2673

Powder X-ray diffraction patterns of Ag_6O_8AgX ($X=NO_3$, HF_2)



Single crystalline samples.



We succeeded in synthesizing single crystalline samples of $Ag_6O_8AgNO_3$ and $Ag_6O_8AgHF_2$.

Normal state of $Ag_6O_8AgNO_3$ and $Ag_6O_8AgHF_2$

$Ag_6O_8AgNO_3$

$Ag_6O_8AgNO_3$ shows phase transitions near 90 K and 180 K.

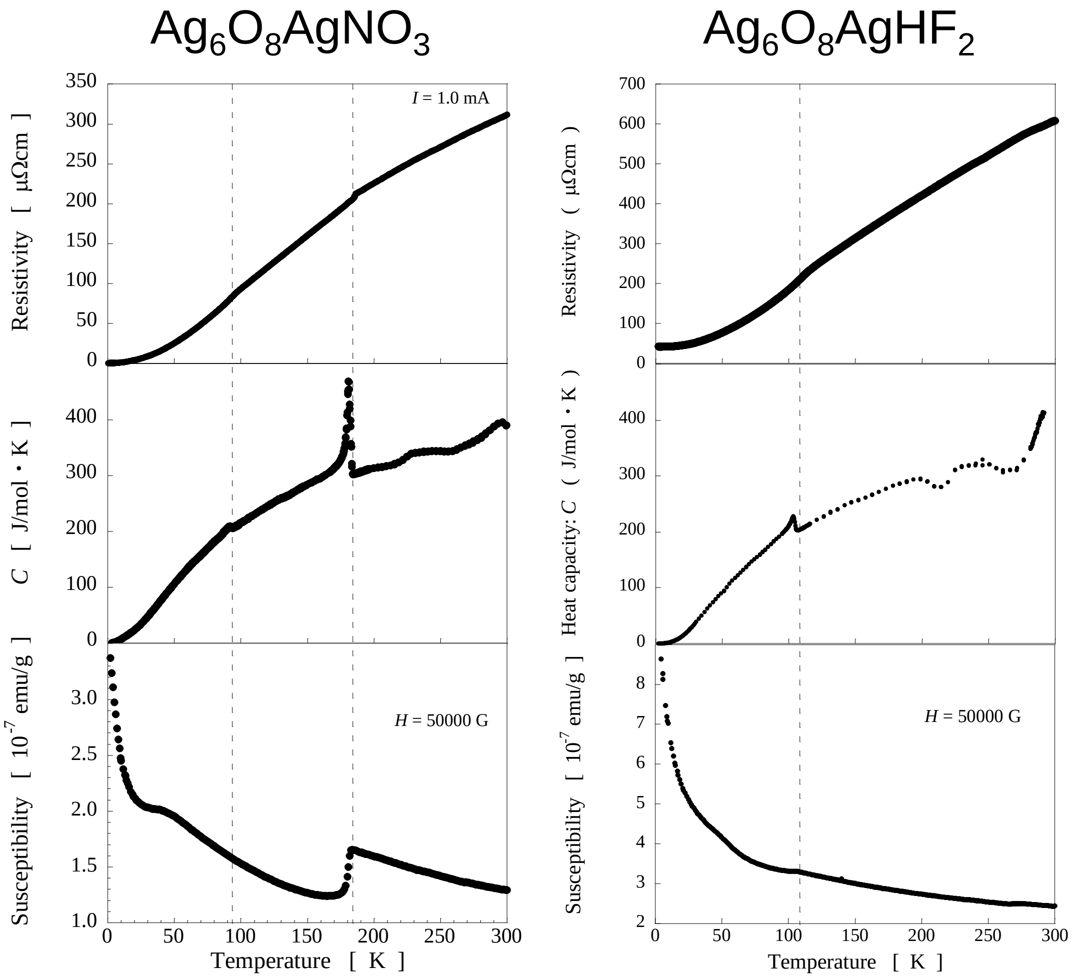
180 K: Structural phase-transition from Cubic to Tetragonal.

(We confirmed this transition using X-ray diffraction).

90 K: Small phase transition: stopping of NO_3^- ions rotation?

$Ag_6O_8AgHF_2$

$Ag_6O_8AgHF_2$ shows phase transition near 110 K. We consider that this transition is generated by stop of HF2- ions spin like $Ag_6O_8AgNO_3$ material.



$Ag_6O_8AgNO_3$

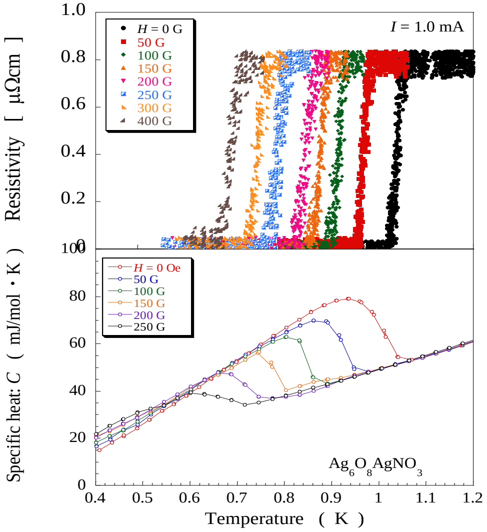
$Ag_6O_8AgHF_2$

Superconducting state of $Ag_6O_8AgNO_3$ and $Ag_6O_8AgHF_2$

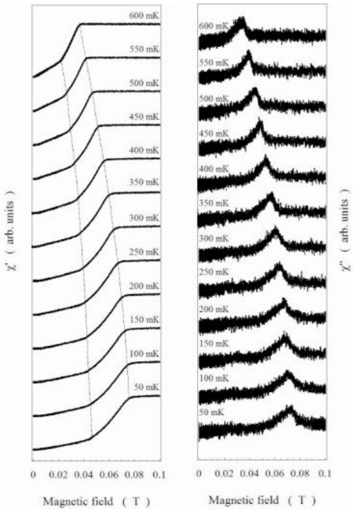
$Ag_6O_8AgNO_3$

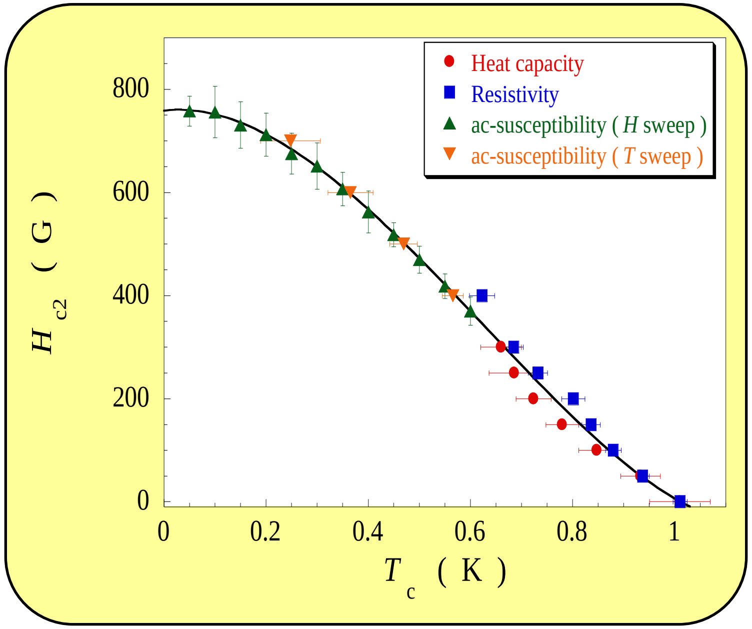
$Ag_6O_8AgNO_3$ shows superconducting transition at 1.04 K as described in a previous report. We determine a upper critical field: H_{c2} to be 770 Oe and calculated coherence length: ζ to be 42.5 nm.

Resistivity & heat capacity.



ac-susceptibility.





$Ag_6O_8AgHF_2$

We confirmed superconducting transition at 1.5 K more clear than previous report and performed some measurements to elucidate superconducting state in $Ag_6O_8AgHF_2$.

Summary

- Electron doped (La, Nd-doping) 14-24-41 system
  - M-I transition is observed in both system
  - S~0 is observed in Nd-doping
- Two gap superconductivity in Y_2C_3 (from NMR & SpHeat).
- New type-I superconductivity in B-doped SiC.
- First information for H-T phase diagram by single crystalline Ag-clathrate system

With struggling, struggling,

***T*$_c$ is getting decreased !!**

Finally, how T_c is determined ?

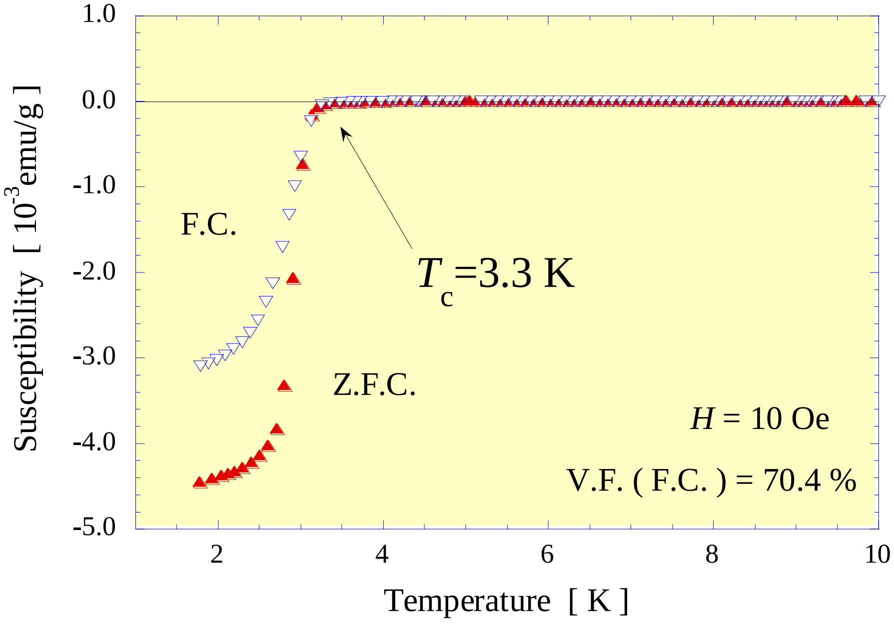
T_c = (Luck) × (Spirit) × (Idea)

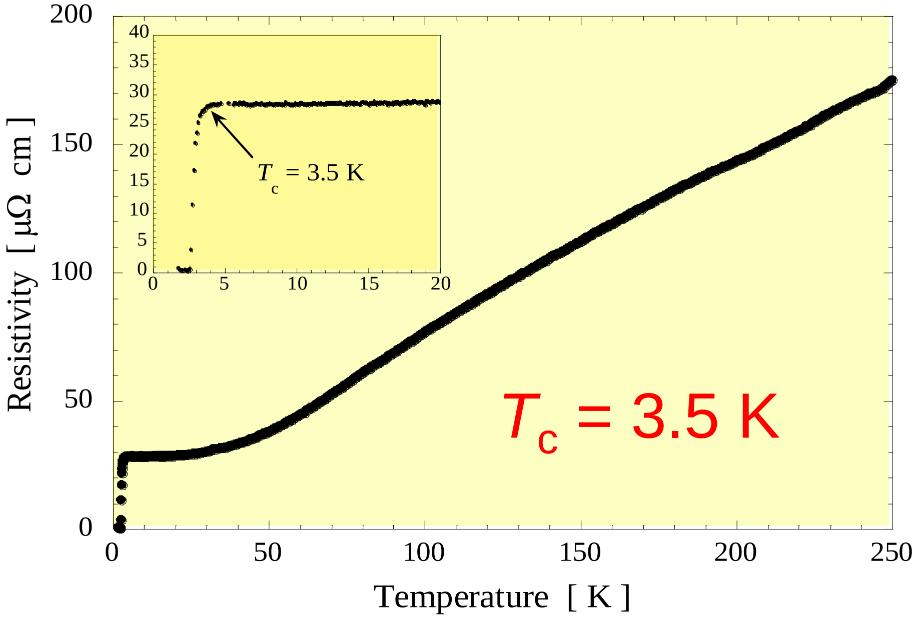
Searching for New superconducting intermetallic compounds

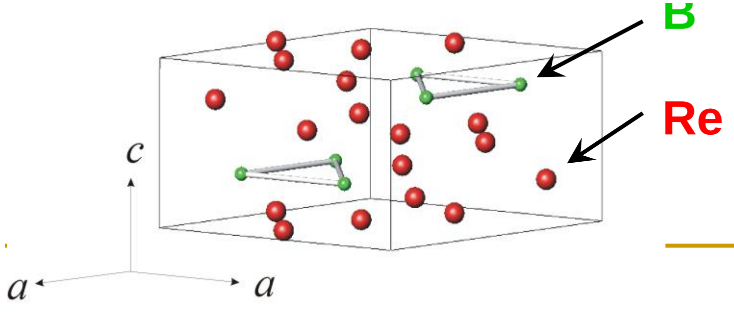
Re_7B_3	(T. Muranaka, A. Kawano)
Re_3B	(T. Muranaka, A. Kawano)
$(W,Mo)_7Re_{13}(B,C)$	(K. Kawashima, A. Kawano, T. Muranaka)
W_5Si_3	(S. Akutagawa, Y. Kanai, T. Muranaka)
Rh_2Ga_9	(K. Tanaka, S. Akutagawa)
Ir_2Ga_9	(K. Wakui, S. Akutagawa)
NaAlSi	(S. Kuroiwa, H. Kawashima, H. Kinoshita)

Aoyama-Gakuin
University

Physical properties of Re_7B_3







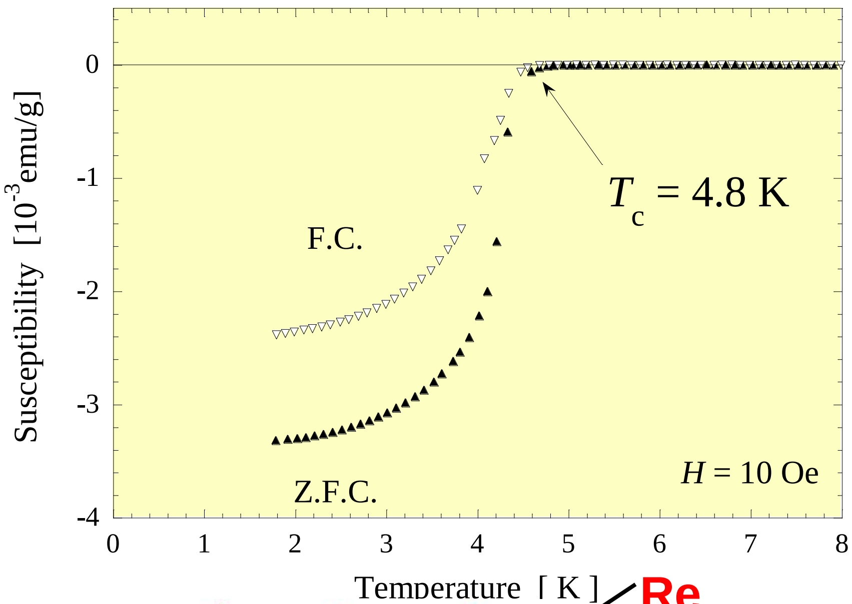
Hexagonal
$P6_3/mc$

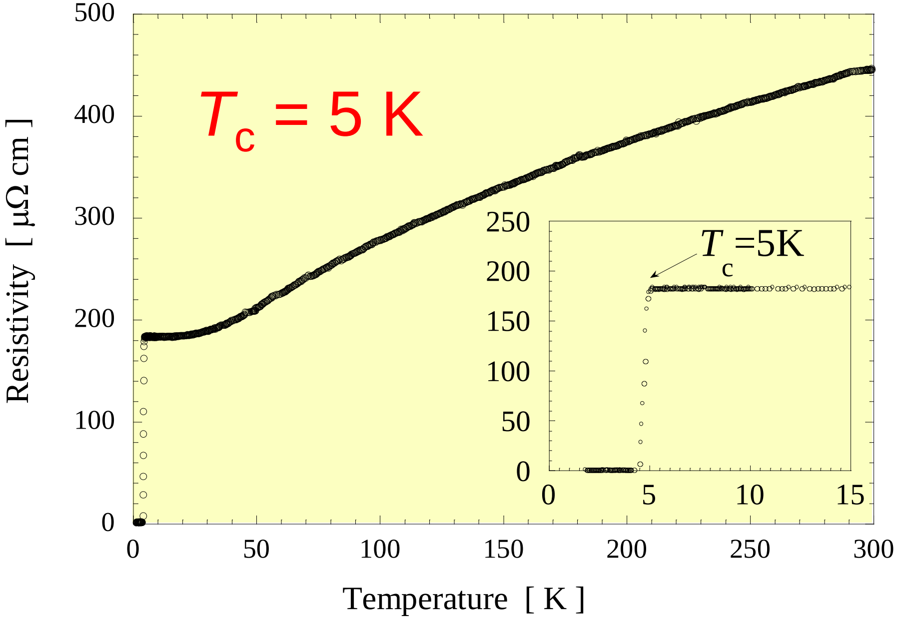
a = 7.504 Å
c = 4.881 Å

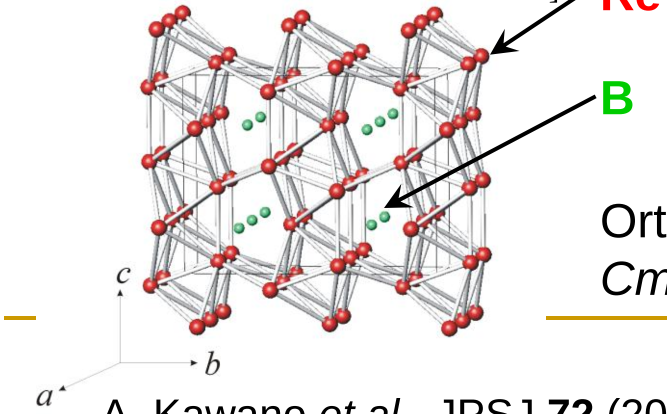
A. Kawano *et al.*, JPSJ **72** (2003) 1724.

Aoyama-Gakuin University

Physical properties of Re_3B







Orthorhombic
Cmcm

a = 2.890 Å
b = 9.313 Å
c = 7.258 Å

A. Kawano *et al.*, JPSJ **72** (2003) 1724.

Superconducting properties of Re_3B, Re_7B_3

	Re_3B	Re_7B_3
T_c [K]	5.0	3.5
H_{c1} [mT]	8	6
H_{c2} [T]	5.2	1.8
λ [Å]	2870	3310
ξ [Å]	80	135

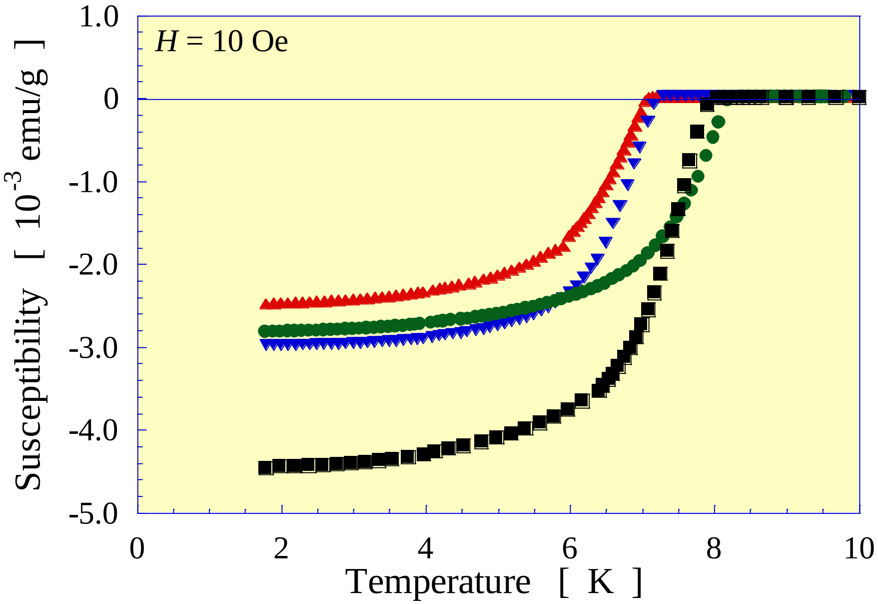
From Specific Heat measurement of Re_3B

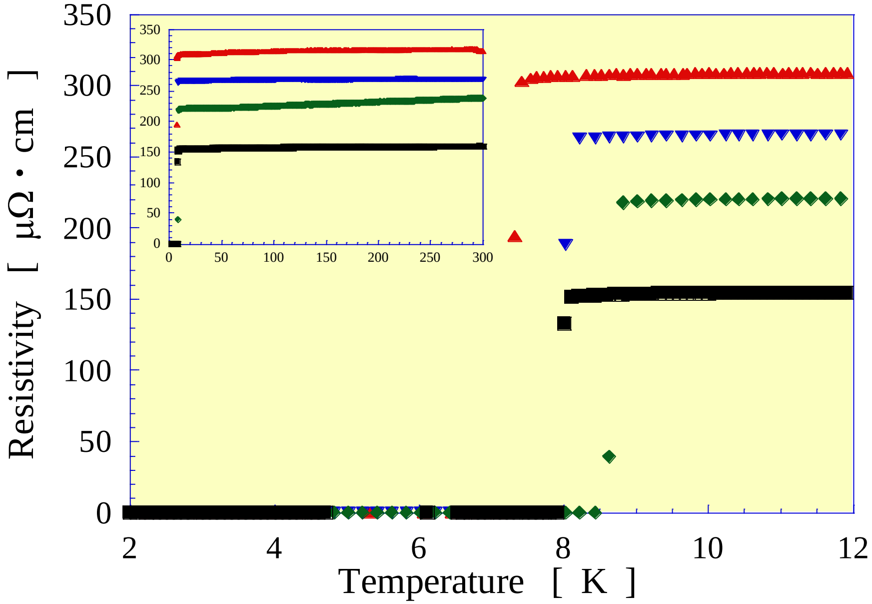
$$2\Delta_0 / k_B T_c = 3.53, \ \Delta C / \gamma T_c = 1.92$$

Weak coupling s-wave superconductor

A. Kawano *et al*., JPSJ **72** (2003) 1724

Physical properties of $(W,Mo)_7Re_{13}(B,C)$





▲ **$W_7Re_{13}B$**

▼ **$W_7Re_{13}C$**

◆ **$Mo_7Re_{13}B$**

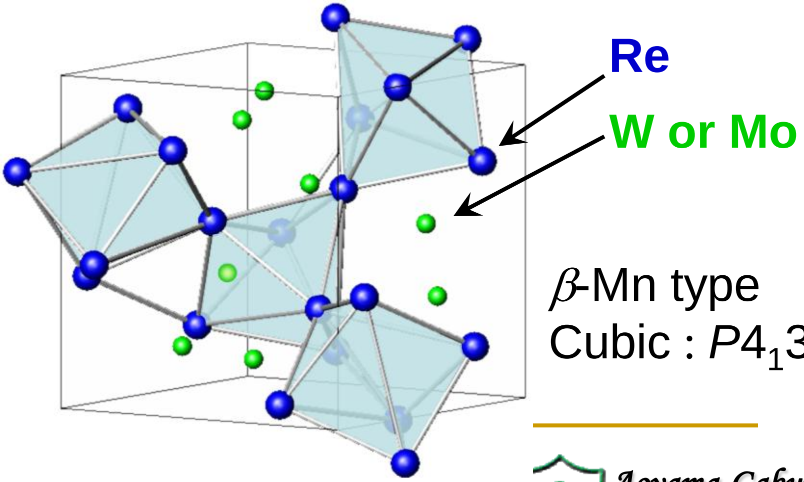
■ **$Mo_7Re_{13}C$**

$W_7Re_{13}B$: T_c = 7.2[K] *V.F.* = 61 %

$W_7Re_{13}C$: T_c = 7.3[K] *V.F.* = 73 %

$Mo_7Re_{13}B$: T_c = 8.1[K] *V.F.* = 58 %

$Mo_7Re_{13}C$: T_c = 8.0[K] *V.F.* = 81 %



β-Mn type
Cubic : $P4_132$

K. Kawashima *et al.*, Physica B **378-380** (2006) 1118.

Aoyama-Gakuin University

Superconducting properties of $(W,Mo)_7Re_{13}(B,C)$

	$W_7Re_{13}B$	$W_7Re_{13}C$	$Mo_7Re_{13}B$	$Mo_7Re_{13}C$
T_c [K]	7.2	7.3	8.3	8.1
H_{c1} [mT]	7.7	4.0	3.0	3.1
H_{c2} [T]	11.4	12.6	15.4	14.8
λ [Å]	2925	4060	4684	4608
ξ [Å]	54	51	46	47

From Specific Heat measurement of

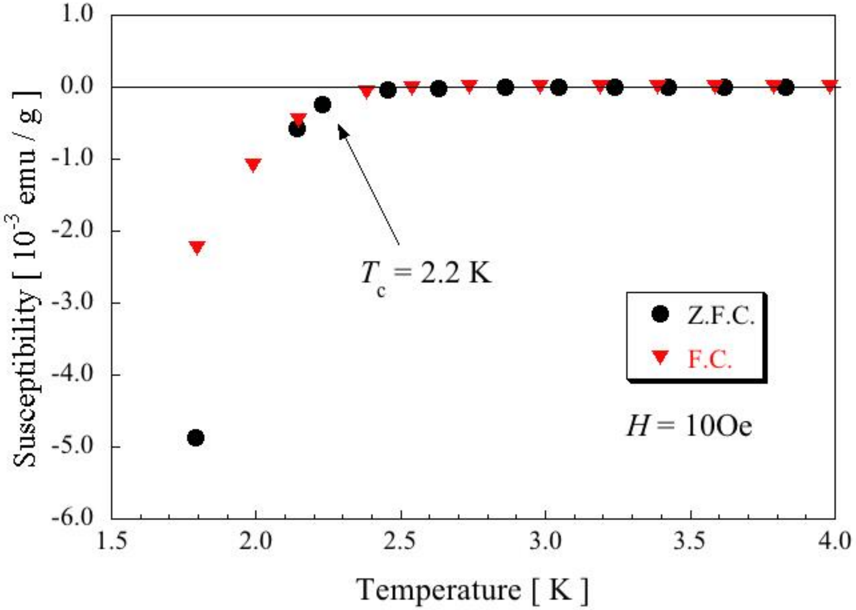
$W_7Re_{13}(B,C)$ and $Mo_7Re_{13}(B,C)$

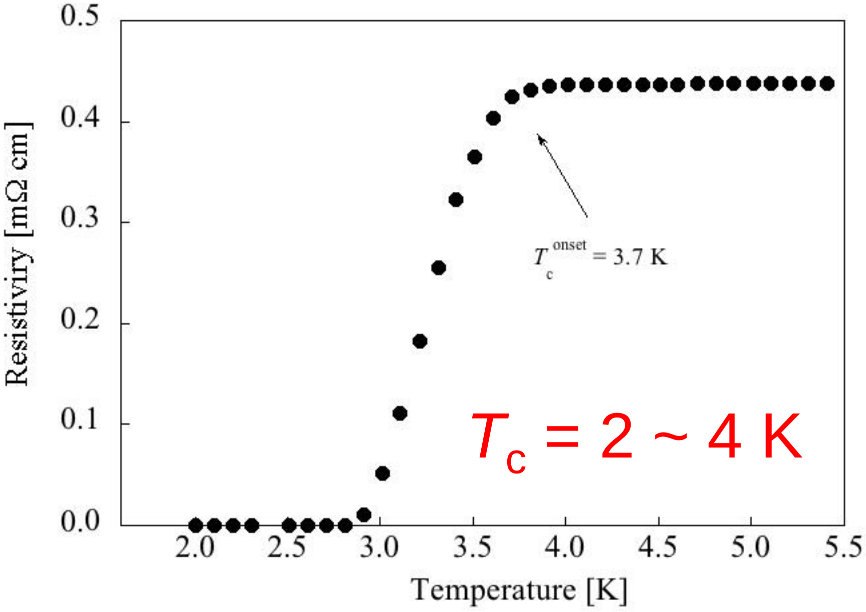
$2\Delta_0 / k_B T_c$ = 4.2, 4.0 and 4.4, 4.2

Strong coupling s-wave superconductors

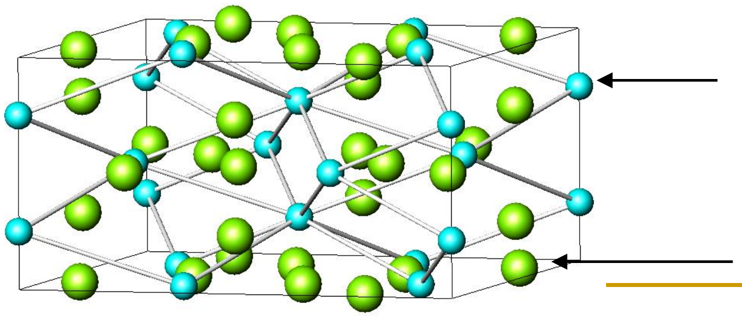
K. Kawashima *et al*., JPSJ **74** (2005) 700.

Physical properties of W_5Si_3





T_c = 2 ~ 4 K



Si

W

*I*4/*mcm*

a = 9.645Å

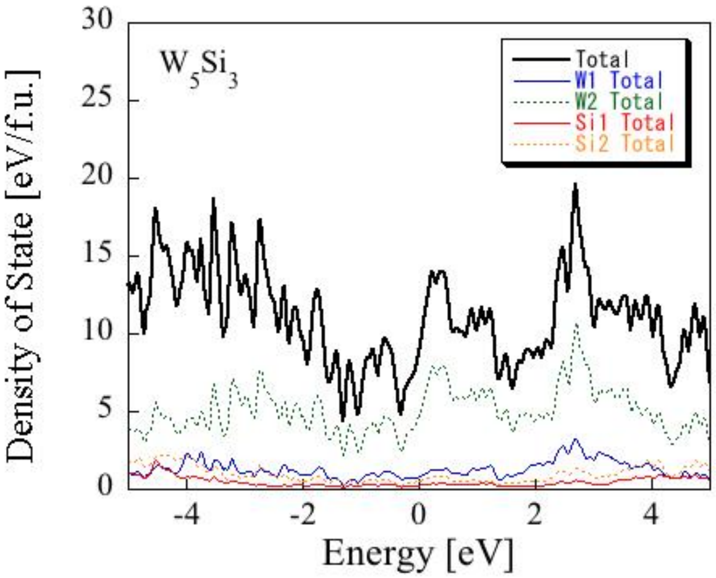
c = 4.97Å

S. Akutagawa *et al.*, to be published in Physica C.

Superconducting properties of W_5Si_3

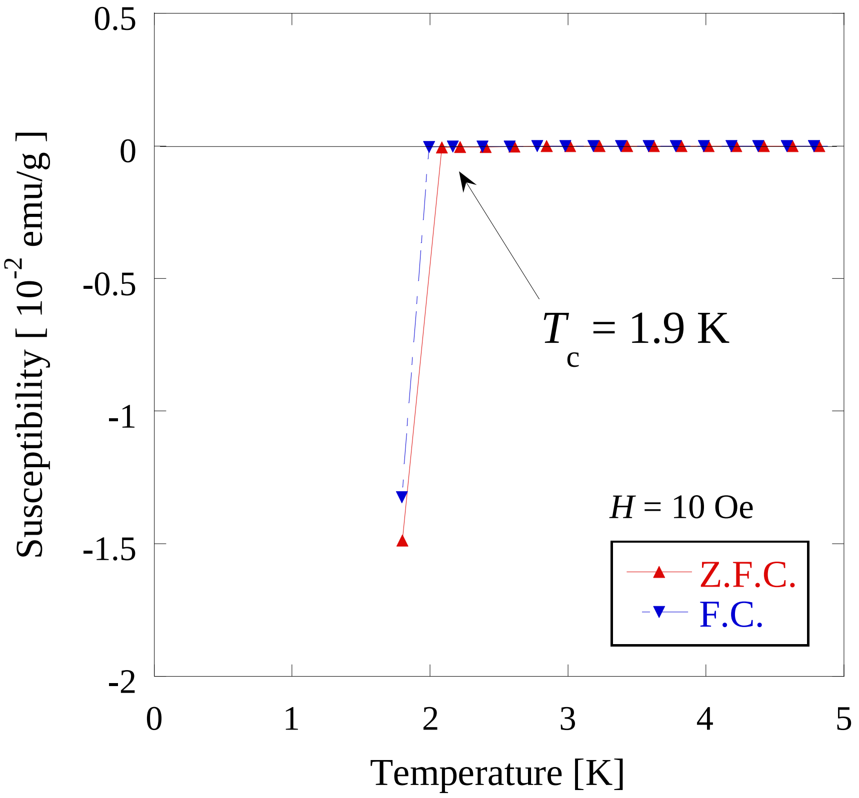
T_c [K]	2.8
H_{c1} [mT]	1.5
H_{c2} [T]	2.6
λ [Å]	5737
ξ [Å]	113
γ [mJ/mol K^2]	14.8
Θ_D [K]	66.6

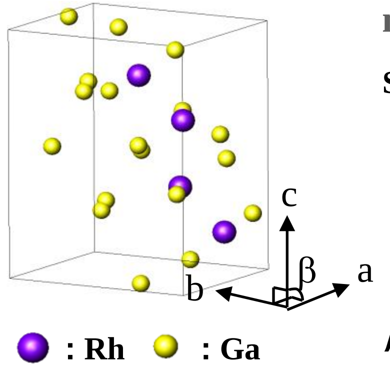
Calc. DoS



- Type-II superconductor
- DoS at EF is mainly contributed from W orbital.

Physical properties of Rh_2Ga_9





monoclinic

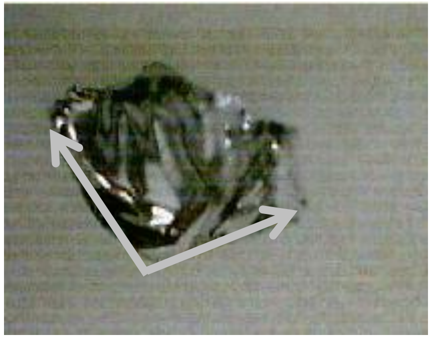
Space group : Pc

a = 6.4164 Å

b = 6.4119 Å

c = 8.7847 Å

β = 93.39° [1]

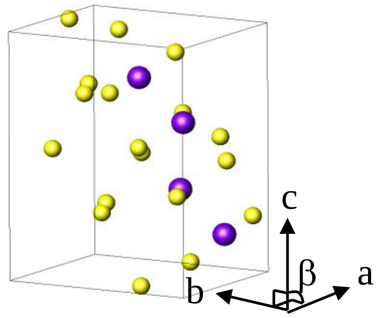


Size of single crystal : 1.8mm × 1.5mm × 1.2mm

---

[1] M. Boström *et al.*, Zeitschrift fuer Anorganische und Allgemeine Chemie **631(2-3)** (2005) 534-541.

Physical properties of Ir_2Ga_9



● : Ir ● : Ga

monoclinic

Space group : Pc

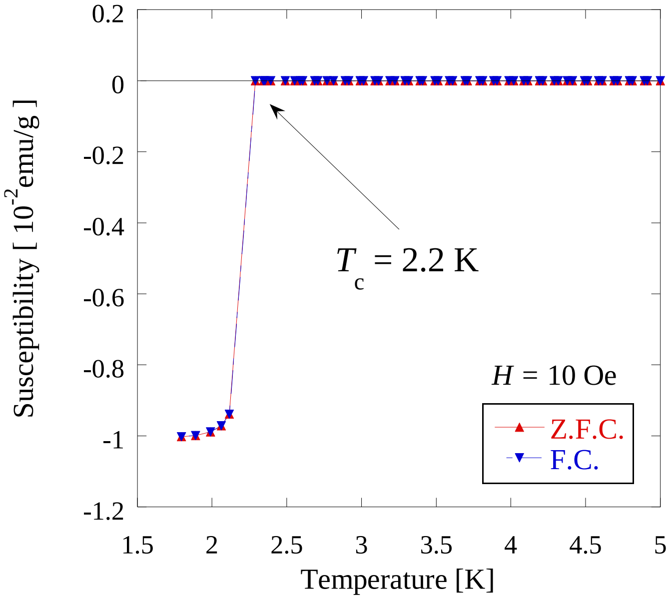
***a* = 6.4329 Å**

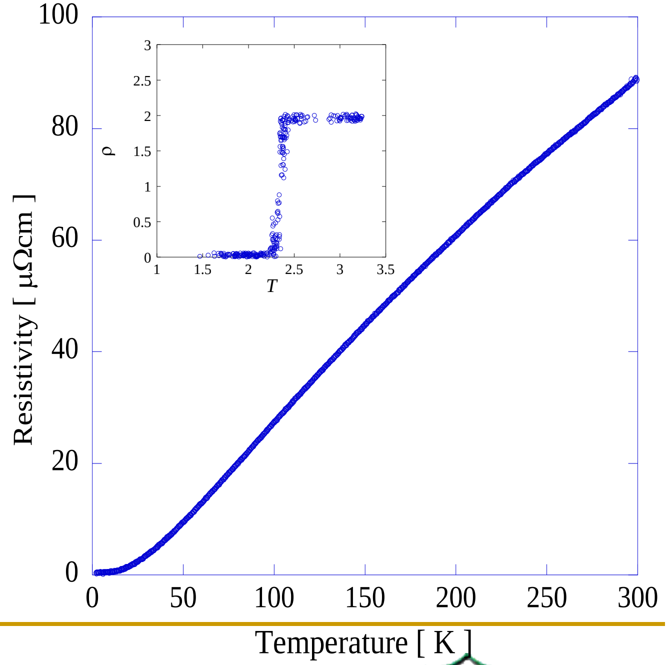
***b* = 6.4099 Å**

***c* = 8.8068 Å**

***β* = 93.464˚**

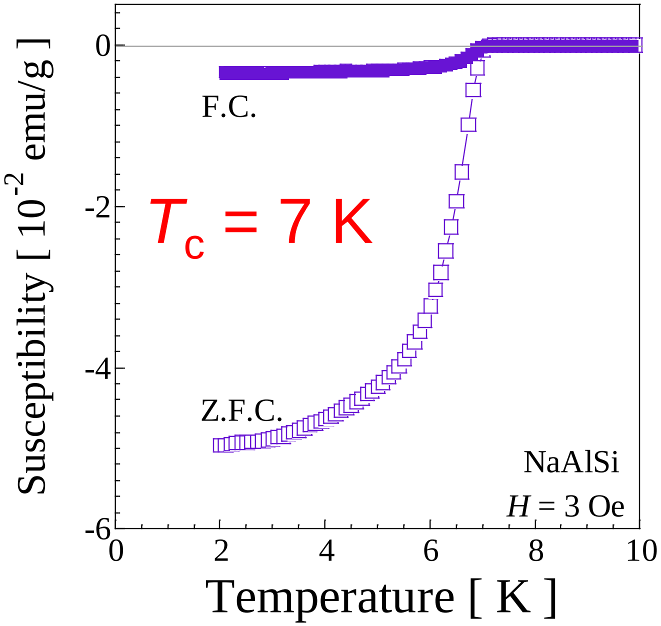
Size of single crystal : 2mm × 1.5mm × 0.5mm

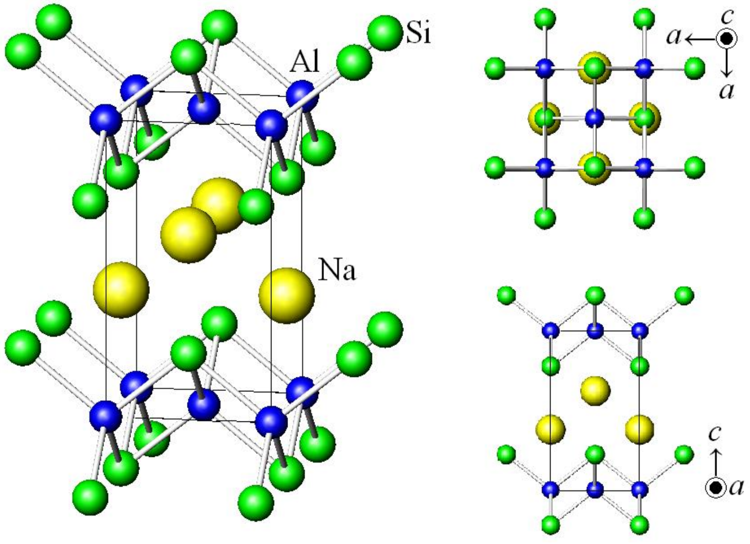




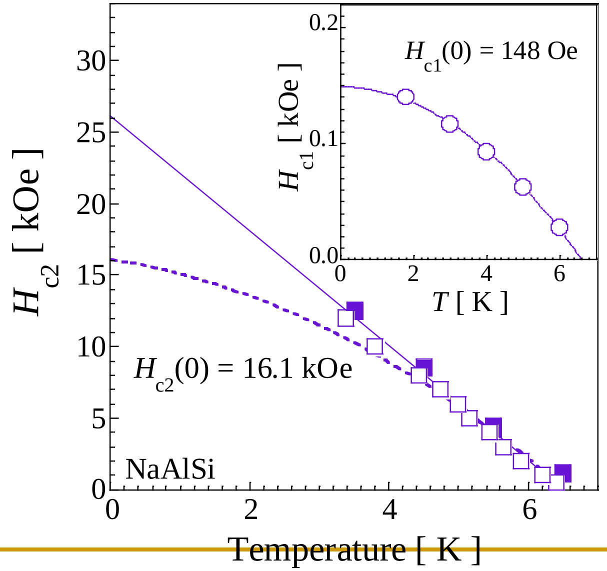
Aoyama-Gakuin University

Physical properties of NaAlSi





Crystal Structure (*P*4/*nmm*, No. 129, Z = 3)



S. Kuroiwa *et al*., submitted to J. Phys. Soc. Jpn.